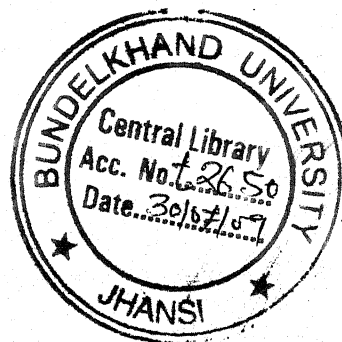


# NON EQUILIBRIUM THERMODYNAMIC BASED TRANSPORT STUDIES ACROSS THE MODEL MEMBRANES



*Thesis*  
*Submitted to the*  
*Bundelkhand University, Jhansi*  
*for the degree of*  
*"Doctor of Philosophy"*  
*in*

*PHYSICS*

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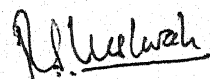
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### **CERTIFICATE**

This is to certify that the thesis entitled "***Non Equilibrium Thermodynamic Based Transport Studies Across The Model Membranes***" submitted by Ramesh Babu Sharma for the award of degree of "***Doctor of Philosophy***" in physics based on the results of experiments carried on by him under my supervision. The candidate has put more than 200 days in the department as required by university ordinance. The thesis or a part thereof has not been previously submitted for the award of any degree is forwarded to Bundelkhand University, Jhansi.

Date : 20 Aug '05

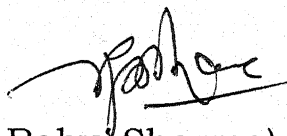
  
(R.S.Kushwaha)



## **DECLARATION**

I hereby declare that the thesis entitled **"Non Equilibrium Thermodynamic Based Transport Studies Across The Model Membranes"** being submitted for the degree of **"Doctor of Physiology"** to the Bundelkhand University, Jhansi (U.P.) is an innovative piece of work carried out by me with utmost dedication and to the best of my knowledge and belief, it has not been submitted else while.

Date : 20 Aug'05

  
(Ramesh Babu Sharma)

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## GENERAL INTRODUCTION

Membrane science is the multi disciplinary field of research. Physics, Chemistry, Maths and Biology etc. Contribute to the investigators for carrying out the work regarding the characterization of model and biological membranes.

Joint applications of physics and mathematics in the form of derived theoretical equations are being utilized in the evaluation of theoretical thermodynamic membrane parameters. When theoretical results co-inside with the experimentally observed membrane values, then existence of theories as well as of membranes both are confirmed. In fact, non equilibrium thermodynamic based equations like- Kederm-Catchlasky equations, Teorell- Meyer - Sievers (TMS) theory, Nernst - Plank system of equations, equations of absolute reaction rate etc. are being used to carry out the electro chemical studies of the membranes, Mechanics, and thermodynamics in membrane permeation and the physics of electrical effect and energy conversion in membranes are main focus of physics dependence. Moreover, author would like first to present more about membranes before saying anything.

Transport processes occuring across artificial membranes separating different solutions have attracted the attention of chemists, chemical engineers and biologists etc. Chemists and chemical engineers would like to understand the mechanisms of transport so that with the knowledge so gained they would be able to fabricate membranes of any

desired property or properties. Biologists, however, would like to use them as simple models for the physiological membranes in order to understand the behavior of complex cell membranes in terms of established physicochemical principles. The recent progress pertaining to membrane diffusion and transport problems have been achieved in varying fields like Chemistry, Bio chemistry, Physiology, Pharmacology, Biophysics, and Industrial Chemistry etc. in which the starting points and aims have been different. Surface chemistry, Solution theory, colloid chemistry, electrochemistry and thermodynamics etc. have been employed to understand the mechanism of transport in living cells, Desalination and Electrodeics. There are several areas of membrane research which have potentially far-reaching consequences to medicine and chemical industry. Work in this field is contributing significantly to the economic prosperity and physical well being of all mankind.

The literature in book form describing membrane technology and applications is far too extensive to mention. The principal volumes containing significant sections on, or totally devoted to membrane electrochemistry are by Clarke and Nachmansohn (1), Helfferich (2), Spiegler (3,4), Merten (5), Marinsky (6), Stein (7), Cole (8), Lakshminarayanaiah (9-11), Hope (12), Arndt and Roper (13), Polenskey (14), Kotyk and Janacek (15) and others. Continuing series are edited by Bittar (16), Eisenman (17), Danielli, Rosenberg and Cadenhead (18). Applications of membrane electrochemistry to yield activity sensing electrodes are amply described in books edited by Eisenman (19) and

Durst (20). Moreover, some recent literature in book form, as "Membrane Technology" is reported by Baker (21), Nunes (22) and Mallevaile et al. (23). However, this field has produced such a variety of new measuring devices and also has opened so many analytical possibilities in terms of new analysis and new detection systems that it is very likely that additional volumes will soon appear. Numerous recent volumes are concerned, in part, with membrane electrochemistry (24-32).

Polymeric membranes have been used for water deionization for over three decades. With the development of carefully designed membranes with prescribed pore structure and charge density, it is now possible to selectively separate mono and multivalent ions. Water hardness is due to the presence of divalent ions of calcium and magnesium. The traditional method for water softening includes lime-soda and ion exchange processes. Membrane softening is becoming an alternative to these processes (33).

On the other hand, charged membranes have been extensively applied in many fields. In particular, cation and anion exchange membranes have been mainly used for salt enrichment from sea water by electro dialysis on the industrial scale. At present, a further development of the charged membrane system with new functional groups is required to increase the efficiency in the desalination of sea water or to recover waste solutions containing heavy metals. Actually, the developmental research on electrodialytic desalination using ion exchange membrane was initiated in United States and Europe in the 1950s to obtain potable

water from brackish water. At about the same time, research into sea water concentration for obtaining salt was initiated in Japan. Presently, seven companies produce 1.3 million tons of edible salt per year using ion exchange membranes. As it is known that the internal energy of thermodynamic system can change as a result of heat, exchanged between the system and its environment and work done by or on the system. Since thermodynamic development from studies on the heat engine, the system considered was, as a rule, a gas in a cylinder closed by a piston that could move allowing energy to be exchanged as volume work, whose differential expresses as  $p dv$ . If no external forces are present, such work is the only one that a homogeneous system can do, and obviously, it is a far energy from what is happening in nature. Work and energy conversion that occur around us and within us have nothing to do with volume changes, save for the ubiquitous heat engine. In living organism, the chemical, electrical, and osmotic work is performed. A thermodynamic system can do such types of work at the expense of its free energy only when external forces are present. Such forces are transmitted to the system via the biological membranes, which is a ubiquitous contrivance that surrounds all living cells and cell organelles and has the form of a lipid bilayer with embedded integral and peripheral protein molecules. Now, after having focused on some applications of membrane technology, author would like to express the definition of membranes as follows:



A precise and complete definition of the word "Membrane" is difficult to make (34), and any complete definition given to cover all the facets of membrane behavior will be incomplete. According to Sollner (34,35) "A membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the latter, but permits passage, with various degrees of restriction, of one or several species of particles from the one to the other or between the two adjacent phases or compartments, and which thereby acting as a physicochemical machine transforms with various degrees of efficiency according to its nature and composition of the two adjacent phases or compartments. In simple terms it is described as a phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquids and/or vapours contacting the two surfaces (9). The term heterogeneous has been used to indicate the internal physical structure and external physicochemical performance (33,36-38). From this point of view, most membranes in general, are to be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous (39).

The notion of homogeneous vs. heterogeneous membranes proves to be an important distinction from the point of view of mass transport. In the dilute solution limit, the friction coefficients for mass transport by diffusion or migration are interconvertible by Onsager reciprocal relations, and both can be related to jump distances and frequencies

according to random walk models. As long as there are no preferred regions of low friction in the membrane, it is isotropic on a molecular level and is considered to be homogeneous. Uniformity of mesh on a molecular scale is another view of homogeneity. Channel free solid and liquid membranes are usually homogeneous, and two phase membranes such as solid crystallites imbedded in a nonionic resin are clearly heterogeneous. The distinction, however, is not always essential (40).

Membranes may be solid, liquid or gas (41) and the outer phases are usually liquid or solid. Membranes are usually thin in one dimension relative to the other two dimensions. This property is only functional or operational. In order to achieve a measurable chemical change or electrochemical effect and to make chemical or electrochemical measurements on a membrane system in a reasonable time, some transport related property must be susceptible to temporal change. Thus, a change in potential, flux, or concentration (among many varying and measurable quantities) requires membrane thicknesses  $d$  such that  $d^2/2D$  is comparable with the observation time ( $D$  is a mean diffusion coefficient). Although irregularly shaped membranes are conceivable, most theories and experiments are restricted to systems with one dimension, the  $x$  direction in parallel-face, planar membranes or along a radius in membranes with spherical shape.

Membranes are considered to be porous or nonporous depending upon the extent of solvent penetration (42). At the nonporous extreme are membranes which are nonionic and contain negligible transportable

species at equilibrium. Ceramics, quartz, anthracene crystals, and teflon films between metal electrodes or electrolyte bathing solutions are solid membrane examples. Organic liquid films such as hydrocarbons and fluorocarbons in contact with aqueous electrolytes are liquid membrane example. At the other extreme are porous membranes, which can be solvated and will contain components from the outer phases. Among these are nonionic films such as cellophane, inorganic gels, and loosely compressed powders in contact with aqueous solutions. These materials absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. More widely studied are the membranes of polyelectrolytes, aqueous immiscible organic liquid electrolytes (2,9,11,43), various parchment supported inorganic precipitates (44-58), solid ion conducting electrolytes including silver halides, rare earth fluorides, and alkali silicate and alumino-silicate glasses (19,20,59,60). All these materials contain ionic or ionizable groups within the membranes which are capable of transport under diffusive or electric field forces. In addition, these materials possess the property of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion exchangers are surprisingly slow to take up water, while the inorganic salts have no tendency to hydrate. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water (61,-63).

Depending on the dielectric constant and solvent penetration, sites are potentially, partially or even completely ionized. A characteristic of

electrolyte membranes is the presence of charged sites (2, 64-66). If ionic groups are fixed in a membrane as  $-$  and  $+$  attached to cation exchange resins, the membrane is considered to possess fixed sites, even if protons or metal ions are covalently bonded to the sites. In glasses, the fixed sites are  $-$  and  $+$  groups, while in anion exchange resin membranes these are  $-$  and  $N^+$ . On the other hand liquid ion exchangers which are water immiscible such as diesters of phosphoric acid, can be viewed as mobile site membranes. The acid is trapped in the organic phase, while the protons and/or other cations can move in and out of the membrane, the phosphonate cannot. Membranes without ionizable groups contain no charge sites. It is important to know that cellulose triacetate, which is initially site free, soon develops negative sites by hydrolysis and oxidation on exposure to aqueous solutions.

The frequent use of "charged" and "uncharged" in the membrane literature is usually unsound electrostatically, but does provide an intuitive chemical description. For example, "charged" membrane usually refers to electrolyte membranes such as solid and liquid ion exchangers where the fixed and mobile sites are the "charges". Actually, these membranes are quasi-electroneutral in their bulk when the thickness is large compared with the distance between ions, the sum of ionic charges.  $\sum Z_i C_i = 0$ . In the literature, "uncharged" membranes are those, like cellophane, with no fixed charges. This frequently used literature definition provides no place for lipid bilayer membranes, which are electrostatically neutral only in the absence of charge carriers and in the

absence of bathing solution whose salts possess preferential solubility of anion over cation or vice versa, but are usually electrostatically charged by an excess of ions of one sign in normal operation. Thick hydrocarbon membranes and membranes of biphenyl ether (or derivatives), phthalate, and sebacate esters are generally neutral in the presence of most bathing electrolytes, but may be charged electrostatically, depending on thickness, in the presence of neutral carrier species which preferentially solubilize ions of one sign. The use of "charged" and "uncharged" to describe electrolyte or non-electrolyte membranes has been discouraged unless the precise electrostatic connotation is involved (40).

Membranes may be broadly classified into natural and artificial. Natural membranes are classified to possess a fundamental unit membrane structure which is a bimolecular leaflet of lipid with their polar groups oriented towards the two aqueous phases of the cell, and protein is supposed to exist close to the polar heads of the leaflet. This type of the universal structure is absent in artificial membranes. Eisenman et al. (67) have given a classification of these membranes based on their structures.

Unlike the classification based on membrane structure, membranes are usually classified either on the basis of their nature, i.e., coherent gel or otherwise, or on the nature of the chemical reaction involved in their formation, i.e., addition or condensation reaction. The efforts of various workers have been directed towards: (A) preparing membranes with good chemical and mechanical stability and favourable electrical performance suitable for fundamental transport studies and for applications in some

industrial operations such as the treatment of brackish water, saline water conversion, etc., (B) building suitable models to mimic the properties of natural membranes, and (C) preparing composite membranes containing cationic and anionic groups in suitable arrangement to demonstrate and to study the physicochemical phenomena associated with the rectification of alternating current and other special membranes for specific purposes. It is worthwhile to mention that most of the work concerning category (A) seems to be directed towards finding suitable membrane materials for fabricating a structure for effective desalting sea water by application of pressure. The most commonly used material for casting a membrane for desalination is cellulose acetate although, polymethacrylic acid (PMA), phenolsulfonic acid (PSA), polystyrene sulfonic acid (PSSA) and cellulose esters have proved very useful (68). A number of investigators in recent years have prepared membranes from cellulose acetate under varying conditions and used them to understand the mechanism of water flow (3,4,5,69-83). In category (B) bilayer membranes, first generated by Mueller (84), have most widely been used as model for living cells and the studies have given somewhat a better understanding of the structure and function of the natural membranes. The membranes of category (C) are quite numerous (10,40,85-87).

Theories on the transport of charged or uncharged particles across membranes can be roughly divided according to Schlögl (88) into the following groups.

Group one considers the membrane as a surface of discontinuity, setting up different resistances to the passages of the various molecular or ionic species (89-90). The driving forces are the differences of the general chemical potential between the two outer media (Differences of pressure or electrical chemical potential are included in the general chemical potential).

Group two considers the membrane as a quasihomogeneous intermediate phase of finite thickness in which the local gradients of the general chemical potential act as driving forces (64,65,91-97). Convection may also contribute to particles transport within the membrane.

Group three considers the membrane as a series of potential energy barriers lying one behind the other, thus forming, in contrast to group two, an inhomogeneous intermediate phase (98-100). An (irregular) spatial lattice is formed due to the higher probability of finding a particle in the positions between the activation thresholds. The driving forces arise from the differences between the transition probabilities in opposite directions perpendicular to the membranes.

This grouping attempts to classify the various mathematical approaches, according to the ideal models on which they are based. It is in fact too schematic, as many theories occupy intermediate positions. No author is likely to take the view that one of these treatments is right and the others wrong. The various descriptions supplement each other, and depending on the system under consideration, one of the three will prove

the most suitable. It may be shown, for example, that when the number of activation thresholds becomes very large, and the distance between the lattice points sufficiently small, then groups 3 and 2 merge into each other. A transition is also found between group 1 and 2 (88).

Unlike group 3 groups 1 and 2 can be classified in the general scheme of irreversible thermodynamics. In group 1 as well as in group 2, linear relationships are assumed between the particle fluxes and the driving forces. Owing to the differing characters of the driving forces, group 1 is treated according to the method of "discontinuous systems", and group 2 according to that of "continuous systems". An integration in group 2 across the membrane does not as a rule yield a linear relationship between the flux and the general chemical potential difference. Only for sufficiently small differences does group 2 merge into group 1 after integration. In this sense group 2 is more general than group 1. Group 2 is, however, inferior to group 1 in that a number of idealizations must be assumed before an explicit integration can be effected. Kirkwood (101) finds a correction between group 1 and 2. His initial flux equation differs from that normally used in the treatment of "continuous systems" in irreversible thermodynamics. This treatment of Kirkwood has been developed and modified by Schlögl (88). On a broad basis, it may be said that the theories of group 1 are based on the ideas of classical thermodynamics or quasi-thermodynamics which is restricted to isothermal systems. The theories of group 2, apart from being more rigorous and realistic allow a better description and understanding of



transport phenomena in membranes and are useful in dealing with non-isothermal systems. The theories of group 3 provide a general and unified view applicable to systems of differing degrees of complexity. Many of the theories based on the Nernst-Plant flux equation are placed in the first groups whereas those dealing with the principles of irreversible thermodynamics and the theory of absolute reaction rates are placed in the 2nd and 3rd groups respectively.

The theories of the first group have the advantage of being relatively simple. For ion-exchange membranes, however, they are often inadequate. These theories deal chiefly with processes occurring within the membrane. For such a purpose the theories of the second group are proper choice.

The most important theories of the second group are based either on quasi-thermodynamics or on thermodynamics of irreversible processes. The fundamental difference between these two approaches are summarized below.

Quasi-thermodynamics is not interested in particle fluxes. One might say that the quasi-thermodynamic approach consists in taking a snapshot of the system and calculating the emf from the charges which a reversible electric current would produce in the system if it were "frozen" in the state in which the photographic picture was taken. This procedure gives directly the emf of the cell. No model is needed. Taking the snapshot, however, is often not as simple as it may seem. A rigorous treatment would require the knowledge of the composition of every

differential layer of the diffusion zone (i.e., the concentration profiles of all species). Since obtaining this information experimentally is usually too lengthy a task or even quite impossible, the quasi-thermodynamic treatment is forced to make assumption about the condition of the system.

The thermodynamics of irreversible processes (102) in contrast to quasi-thermodynamics, does not require prior knowledge of the concentration profiles. The set of equations of thermodynamics of irreversible processes interrelates all occurring "fluxes" (of species electric current, heat etc.) and "driving forces" (gradients of chemical potential, electric potential, temperature etc.). From measurements of a sufficient number of "phenomenological coefficient," all fluxes, forces, and the emf can be calculated, without knowledge of the profiles and without using the concept of "reversible energy production" on which quasi-thermodynamics is based. Furthermore, thermodynamics of irreversible processes is applicable also to nonisothermal systems and includes coupling of fluxes which is not covered by quasi-thermodynamics. It may be mentioned here that the discipline of irreversible thermodynamics provides a precise mathematical description of the processes of transport and diffusion in membrane systems. Its application to membrane processes is a natural development of the basic theory of onsagar (103) and has been developed by staverman (90), Kedem (106), Katchalsky (102), Caplan (105), Mears (106), Spiegler (3,4,) Rastogi (107), and others in an extensive and expanding literature.

The theory of absolute reaction rate has been applied to diffusion processes in membranes by several investigators. Zwolinski, Eyring and Reese (100) considered the diffusion process as one of the basic phenomena for sustaining the growth and development of plants and organism. They presented a detailed kinetic approach to diffusion which clarifies much established concepts and provide impetus to a fresh approach to the problems in the field of biological diffusion. The absolute reaction rate theory treatment of diffusion and membrane permeability provides a general unified point of view applicable to systems of varying degrees of complexity. It is equally adoptable to the treatment of the permeabilities of membranes to electrolytes, to no electrolytes under the driving forces of a concentration gradient, activity gradient, and external and internal potential gradients. Zwolinski, Eyring and Reese (100) treatise on membrane diffusion is based on the "activated state" or the "transition state" theory.

Laidler and Shuler (99) have also treated the kinetics of membrane transport under steady state conditions. They employ similar principles and express the rate constant of the over all process of surface penetration in terms of a number of specific rate constants. Various special cases are considered and discussed with reference to the experimental data. They developed flux equations for solvent and solute especially as a function of the osmotic and hydrostatic pressures across the mebrane. Recently, Tien and Ting (108) have applied the theory of absolute reaction rates to diffusion processes through Bilayer Lipid Membranes (BLM) and have

derived various thermodynamic quantities like free energy of activation, enthalpy of activation and entropy of activation etc.

Application of electrochemistry in membrane studies is pertinent at three levels (40). One is the development of techniques with application to experimental phenomenology including current-voltage-time-concentration behavior.

A second is the mathematical modeling implied by theory and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties and includes determination of theoretical parameters by electrical methods and by complementary non electrochemical methods : Physical, optical, esr, nmr, Raman, fluorescence, T-jump techniques, etc. From transient and steady state measurement of current or membrane potential as a function of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to modeling beings with the assumption of the membrane as a linear system to which laws of network theory may be applied. Another beings by solution of basic electrodiffusion laws of transport with equilibrium or kinetic boundary conditions in order to deduce forms for system functions which satisfy the data.

In fact the real break through in membranes came in 1970 with the development of reverse osmosis (RO) process for desalination (109) of saline water. In recent years, membrane separation (110) has found large scale applications in several areas starting from desalination water and

waste water treatment, removal of organics from aqueous<sup>u</sup> and non-aqueous systems, chemical vapour recovery, separation of azeotropic liquid mixtures and selective separation of metal ions including rare earths and actinides from process streams. A number of newer developments in membrane processes have taken place, which include development of novel inorganic membranes, such as ionic membrane/bipolar membrane system for electrolytic cell applications and proton conduction ion exchange membranes for low temperature fuel cell application.

The most important contribution of electrochemists to membrane electrochemistry is the transfer of perspective and wisdom to the new area. There are many sine qua nons in electrochemistry which have occurred through extensive studies of electrolytes and electrolyte/membrane interfaces. Electrochemists have learned to subdivide systems into interfacial and bulk processes and to expect effects of dielectric constant (complex formation, ion pairing), effects of short range forces (adsorption of charged and uncharged species with, possibly, changes in rates of interfacial processes), effect of high fields near surfaces (Wien Effect, and dielectric saturation, for example), and the important effect of local potentials on rates of interfacial processes (irreversible charge transfers, psi effects, etc.). Inasmuch as the presence of the space charge at interfaces is a natural consequence of the continuity of potential from one phase to another, the presence of space charge and space charge mediated effects in membrane systems is anticipated.

Armin kargol (112) derived a generalized form of the kedem kachalsky equations describing passive transport through the membrane. A deduction of a relation between transport coefficients of low exchange membranes was carried out by Auclair et al. (113) by comparing the kedem kachalsky and on sager forms of transport equation in the framework of irreversible thermodynamics. In fact, there are six independent Practical Transport Parameters, which permit a complete characterization of ion - exchange membrane (IEM) transport in contact with a single electrolyte : (1) electrical conductivity, (2) transport number of the counterion, (3) diffusion permeability (4) water transport number or electro osmotic permeability (5) hydraulic permeability and (6) staverman reflection coefficient. These parameters enter the kedem kachalsky equations as coefficient that allow fluxes of the electrolyte ions.

In this thesis studies of transport properties of parchment supported inorganic precipitate membranes are reported when they are used to separate various 1:1, 2:1 and 3:1 electrolyte solutions . The membrane electrolyte system has been considered to contain four chemical species, counterion 1, coin 2, water 3 and fourth the membrane matrix which carries fixed ionogenic groups and excludes the possibility of chemical reaction within the membrane. The membrane matrix has, therefore, been considered to consist of fixed charge and adjacent polymer segments which together constitute the repeat unit of the matrix. It is, therefore, possible that kinetic coupling interaction of membrane matrix will

include not only the contribution of fixed charge, but also specific polymer effects if such exist.

This is an important qualification to the description of the species as simple as ion, although it appears from earlier studies that such effects are small (114-116).

The discussion has mainly been restricted for commenting on only a few points concerning the following ionic processes in the membrane systems, "Permeability phenomena".

- 1- Ionic transport "flux"
- 2- Membrane potential
- 3- Electrical conductivity
- 4- Ionic distribution equilibria
- 5- Spatial distribution of ions and the potential within the membrane.

The thesis has been presented under the following heads :

- 1- Thermodynamic Irreversibility : What is it?

Since in the chapter wise discussion, the use of various theories for the evaluation of thermodynamic membrane parameters of parchment supported nickel and cobalt phosphate membranes is based on non-equilibrium irreversible thermodynamics. Therefore, author has tried first to focus his concentration towards the explanation of irreversible thermodynamics by taking some simple and suitable examples. In this regard some diagrams of directional reversibility and irreversibility along with temporal reversibility and

irreversibility are also shown to make the concept of non-aquarium thermodynamics very clear

2- Mechanics of Membrane Permeation:

This chapter of the thesis deals mainly the mechanics of permeation/transport of permeating species across the membranes. The thermodynamic description of membrane transport is supplemented here with the momentum conservation law in the form of the mechanical equilibrium equation. Independently of the way of description, an equation results which contains both mechanics and thermodynamics of membrane permeation. Its usefulness and importance is also demonstrated.

3- Metal-ion selectivity of membranes:

In this chapter author limits his discussions upto the evaluation of meta-lions selectivity of parchment supported nickel phosphate and cobalt phosphate membranes respectively from bi-ionic and multi-ionic potential measurements alongwith conductivity values measured for various 1:1 electrolytes using the different methods. However, membrane energetic parameters derived on the basis of non-equilibrium thermodynamics also support the findings of membrane selectivity for metal ions.

4- Bi-ionic Potential Studies :

The forth and last chapter of the thesis involves the measurements of bi-ionic potential (BIP) of nickel and cobalt phosphate membranes using various combination of 1:1 electrolytes (KCl-NaCl, NaCl-LiCl,



$\overset{C}{K} \overset{C}{Cl} - LiCl$ ) at different concentrations. The intramembrane mobility ratios of metal ions are evaluated using (BIP) values. Moreover, Toyoshima et al. who derived the theoretical equations for bi-ionic potential which contain various parameters, have been evaluated for both the membranes. By substituting these parameters in the equations for bi-ionic potential, the theoretical bi-ionic potentials were calculated at different concentrations. These have been compared with the experimentally observed BIP values. These comparable results are not only the test of theoretical equations but also the test of the membranes for their existence.

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Chatper-I

**THERMODYNAMIC IRREVERSIBILITY:  
WHAT IS IT?**

## Chapter -I

### THERMODYNAMICS IRREVERSIBILITY: WHAT IS IT

#### Introduction & Discussion

Students of thermodynamic (freshman chemistry or physical chemistry) are introduced at an early stage to the distinction between "reversible" and "irreversible" processes. The distinction may be clear enough at that stage, but eventually it turns out to be both puzzling and confusion. Puzzling because no such distinction arises in descriptions of the behavior of underlying molecular models, and confusing because the concept of irreversibility seems to undergo a subtle change after learning about entropy and the second law of thermodynamics. The situation for students was described very well by Duhem 1903 (1) when he referred to reversibility (irreversibility) as "one of the most delicate principles in all of thermodynamics".

And for advanced students, who study the statistical basis for thermodynamics, there is further confusion. The already once-revised concept of irreversibility seems to undergo still another change. Irreversibility becomes a somewhat mystical feature of fluid behavior that has no origin in the underlying molecular mechanics but somehow enters the behavior when we have enough particles to use statistical methods for the prediction of the collective behaviour. This view was summarised explicitly by Montroll in 1961 (2) when he suggested that "we will have to play statistical games in order to extract irreversible characteristics (at the macroscopic level) from the reversible dynamical

equations (molecular level)".

Further, confusion arises for the student who proceeds to the study of the rates of "kinetics" of chemical reaction, electrode processes, and other processes modeled after those (ecological, economic, etc.). In those contexts the terms "reversible" and "irreversible" generally do not have the same meanings they have in thermodynamic contexts, but distinctions among the meanings are seldom made explicit. Compounding the problem are the references to thermodynamic concepts in kinetic arguments about rates. And it is possible to have different kinds of processes going on in the same system. Consider, for example, a cell in which there is a thermodynamically reversible electrode process coupled to a thermodynamically irreversible diffusion process and coupled to a chemical reaction that can be either reversible or irreversible kinetically and, again, thermodynamically. Classifying the cell process is quite a challenge, especially in view of the ambiguity already imbedded in the thermodynamic concepts (3). Fortunately, as we will see below, the kinetic meaning of "irreversibility" is simple and unambiguous.

Thus we have difficulties at various levels in various areas of physical chemistry in understanding exactly what is meant by references to "reversible" and "irreversible". The problem for thermodynamics is composite of simpler kinds of irreversibility that are emphasized with different weights in different applications. To understand thermodynamic irreversibility we have to identify the simpler kinds and the various ways

in which they are mixed. An attempt to do this is developed in the discussion below. More details are available elsewhere (4-7): The problem has been described in another way, which is richer in thermodynamic language by Denbigh (7). Earlier distinctions among kinds of reversibility going back to the turn of the century are reviewed by Heer (8).

### **The Expanding Gas:**

The student of thermodynamics is usually introduced to the distinction between reversible and irreversible processes (9-10) by considering the mechanical work done by one fluid on another before any consideration of the "laws" of thermodynamics. The typical prototype model involves a gas contained in a cylinder with a movable partition that separates the gas at pressure  $p$  from an external fluid at pressure  $P$ . If the pressure  $p$  of the gas is greater than the pressure  $P$  of the external fluid, then the movable, frictionless partition moves to allow the higher pressure fluid (the gas) to expand. The differential work done by the expanding gas of volume  $V$  on the external fluid at pressure  $P$  is formulated as

$$.dw=P dV$$

The expansion process and the work done are said to be "reversible" if  $p$  and  $P$  are equal or nearly equal so that the process can be

reversed by a slight change of  $P$ . It is "irreversible" if  $p$  is substantially greater than  $P$ . In other words the process is reversible if the gas and the external fluid are kept at or near mechanical equilibrium. If they are far from equilibrium during any substantial part of the process, the process is irreversible.

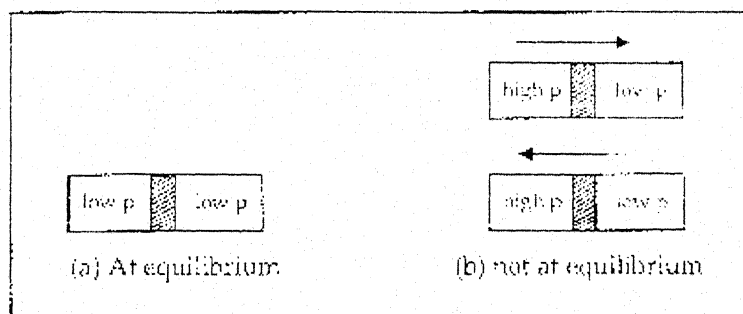
It is generally acknowledged that the concept of reversibility introduced in this way has subtle aspects that are difficult to teach and "elaborate through experiments have been devised to help (11). The problem considered is that of explaining references to "slight changes", "substantially greater", "near equilibrium", etc. and there are other acknowledged difficulties associated, with the neglect of the friction of the movable partition and the shock waves and other deviations from uniformity that arise in irreversible expansions. The difficulties we want to deal with are in another direction. 'We are concerned about the criteria for reversibility and irreversibility.

The criterion for reversibility described above can be stated in a more general way that is often repeated and emphasized by the use of italics in texts, both elementary and advanced (3,9,10). A process is said to be reversible if it can be reversed by a slight change of external conditions (boundary conditions or external forces). If we assume the reversibility defined in this way is clear and simple, then it follows that a process is irreversible, if it cannot be reversed by a slight change of external conditions. Thus the expansion of gas at pressure  $p$  against an

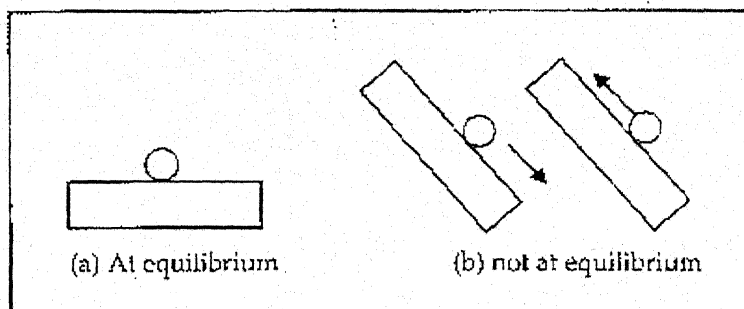


external fluid at lower pressure  $P$  is irreversible because the expansion cannot be changed into a contraction by a slight change of  $P$ .

That criterion for reversibility (irreversibility) described above is clear as applied to the motion of a particle. The "process" (motion) is reversible if it can be reversed by a slight change of external forces (the particle is nearly at "motion equilibrium") and irreversible if the particle has inertia (moving with substantial speed). But, as applied to the expanding gas, the criterion fails to capture the aspect of irreversibility that is purely "thermodynamics" and not simply "inertial".



**Fig. 1 BALL ROLLING ON BOARD**



**FIG. 2 FLUID EXPANDING AGAINST FLUID**

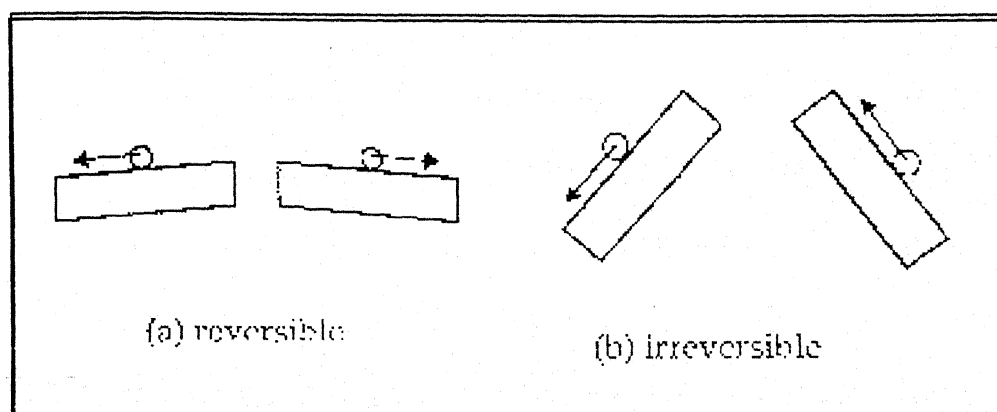


FIG. 3 FLOAT FLOWING THROUGH BAR

In discussions of the second law of thermodynamics (10,12), the emphasis, before considering equilibria, is on the fact that the ongoing fluid process is not only ongoing but is also going in a particular direction, the direction that creates entropy. When the student encounters the second law, he or she is introduced to a "directional" kind of irreversibility that is not implied by earlier explicit definitions of irreversibility based on nearness to equilibrium. He or she does later encounter contexts that seem to combine directional and equilibrium irreversibilities and to take them as logically equivalent. If the student is puzzled at that point, he or she should be puzzled. There are two kinds of irreversibility in the context, and they should be distinguished explicitly.

To illustrate the problem, we compare particle processes with fluid processes. We will find that assumptions that are tacit for fluid processes do not hold for particle processes and require recognition and explanation. Fluid processes, after all, are supposed to be emerged reflections of the behaviour of collections of particles.

Consider, for example, the predicaments of a ball rolling on a board. In figure 1 (a) we have a ball with no initial velocity sitting on a horizontal board. It is at "motion equilibrium". If it were not at equilibrium and moving on a tilted board, as in figure 1(b), it would be undergoing an reversible process when reversed by a slight change of external conditions but the process would be reversible in the directional sense. Depending on its initial conditions, the ball could be moving up the board or down the board. Its "process" would be inertially irreversible but directionally reversible.

On the other hand, if we go back to the expanding gas, we find a different classification of predicaments. If the gas fills the left part of the container pictures in Figure 2(a) and it is separated by a movable wall from an external fluid at the same pressure  $p$ , there will be no movement of the separating wall. The system as a whole is at "mechanical" equilibrium. But if the gas is at higher pressure than the fluid on the right, as in Figure 2(b), then it will start to and continue to, expand. The expansion direction for the process is allowed while the contraction direction is excluded. Here we have a kind of directional irreversibility that was not present in the situation of the ball in Fig.1 (b).

To illustrate further the "directional" irreversibility of fluid processes in contrast to the directional reversibility of the ball-rolling process, we consider another fluid process, heat conduction, described in Figure 3. The equilibria situation pictured in Figure 3(a), where the

temperatures on both sides are the same and there is no initial heat flow, is analogous to the equilibrium situation pictured in Figure 1 (a). But the non equilibrium situation of Figure 3(b) is not analogous to what we have in Figure 1 (b), for one of the directions is not allowed. The exclusion of one of the directions for the fluid processes described by Figure 2(b) and 3(b) represents a kind of directional irreversibility that is missing in the ball-rolling process of Figure 1 (b).

The irreversibility of our expanding gas certainly includes a component that is not implied by merely saying that the process is not at equilibrium. And that component shows up in all fluid process, not just the expansion of one fluid against another or in the conduction of heat from a hot place to a cold place. Evidently we need to recognise different simple kinds of irreversibility before, we can hope to identify the overall irreversibility of fluid behaviour, i.e. "thermodynamic irreversibility". ,

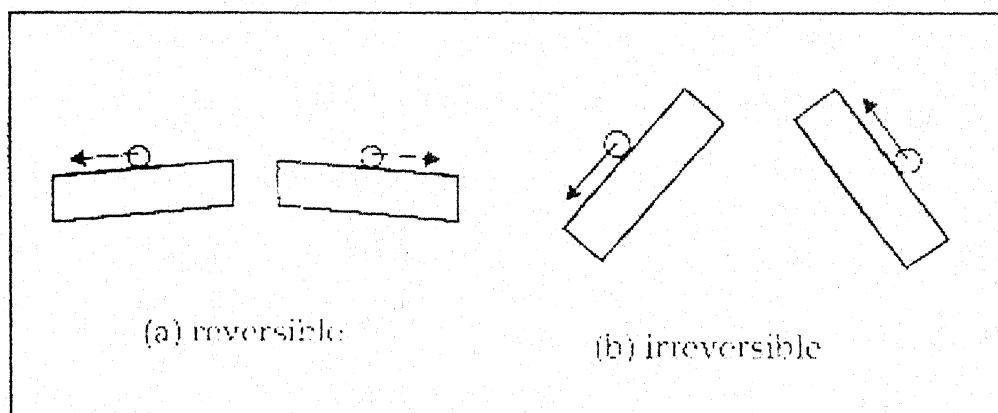
### **Simple Kinds of Irreversibility:**

We consider again the things that can happen when we have a ball rolling on a board (inclined plane). The "external conditions" are determined by gravity and the tilt of the board. The "internal" conditions are the initial conditions, i.e. the initial velocity of the ball. One thing we know from particle( or ball) mechanics is that a moving ball has a inertia and its motion can not be reversed immediately by a change of external conditions(tilt of the board). The process has "inertial irreversibility". If it

started with no or small velocity on a board that is horizontal or tilted only slightly, it would have no or nearly no inertia, and its motion would be reversible in the sense that it could be reversed by a slight change of the tilt of the board. The ball would be at "motion equilibrium" with no (or nearly none) inertia. We could of course, relax the restriction to a "slight" change in the tilt of the board and refer to "any" change if we remember to keep in mind the special case of equilibrium where the board is horizontal. We are led to a criterion for reversibility (irreversibility) that can be started as follows:

**Inertial reversibility:-**

A process is reversible if it can be reversed by a change of external conditions.



**FIG. 4 INERTIAL REVERSIBILITY AND RREVERSIBILITY**

The idea of inertial irreversibility is illustrated by Figure 4. On the left side we have a ball starting slowly down in incline (downward to the left) being changed to a ball moving slowly to the right after the

inclination of the board is changed. The process is inertially reversible. The board is tilted only slightly because we want to emphasize the possibility of equilibrium. On the right side we have a ball moving down the board with substantial inertia that is reduced but not reversed by a change in the inclination of the board. The "process" illustrated on the right side has "inertial irreversibility". ( The tilt of the board is arbitrary because we are not trying to allow for the special case of equilibrium). We do have a problem with our terminology here, which will carry over to analogies with fluid processes. Suppose we have a motionless ball on a tilted board. For completeness in our discussion we want to say that its "process" (subsequent motion) is "inertially" irreversible, which is, strictly speaking, not correct, although inertial irreversibility will soon develop. In a similar way we are going to describe the expanding gas process as "inertially" irreversible, which is not exactly correct at the beginning of the expansion, as described above, even though inertial irreversibility will develop. These special cases have led us to look for a term better than "inertial", a term that is more inclusive, but we have not found the term and are stuck with "inertial" as a term to distinguish between "near equilibrium" and "away from equilibrium".

The idea of "directional irreversibility", as described above, requires no further elaboration. The formal criterion can be stated for directional reversibility as follows:

### Directional reversibility:

A process is reversible if it can occur in both directions under the prevailing circumstances, i.e., if it can be reversed experimentally by changing internal conditions without changing external conditions.

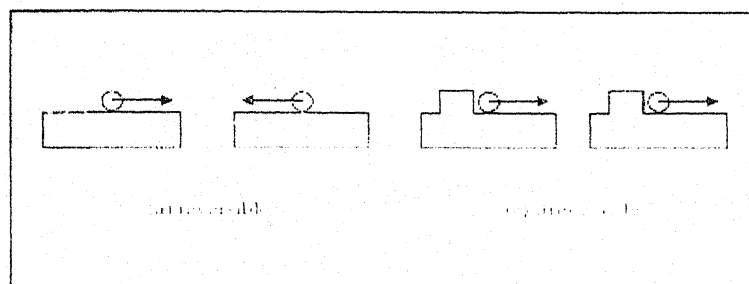


FIG. 5 DIRECTIONAL REVERSIBILITY AND IRREVERSIBILITY

This idea is illustrated in Figure 5. The external conditions for Figure 5(a) involve only the board and gravity. In Figure 5(b) we have added a reflecting obstacle. (We could allow for some space between the ball and the obstacle.) In Figure 5(a) we see the process reversed by reversing the initial velocity of the ball, which is a change of "internal" conditions. In Figure 5(b) we notice the reflecting obstacle on the left side and notice that the ultimate motion of the ball is always to the right and that result cannot be changed by reversing the initial velocity. We may say that the process has directional irreversibility in a conceptual sense. It is irreversible "a priori". Is there an analogue for fluid behaviour? The answer, of course, is negative. So far as we know or can imagine, fluid behaviour is conceptually reversible without mechanical obstacles.

There is one other simple kind of irreversibility that must be noticed here before we return to the expanding gas and try to move on to other processes that have thermodynamic irreversibility. We refer to "temporal irreversibility", which has been promoted in the literature of statistical thermodynamics as the kind irreversibility, that is, the essential component of thermodynamic irreversibility. The idea of temporal reversibility is that reversing motion and not time leads to the same result as reversing time and not motion so that reversing both time and motion leads to a cancellation that leaves the process unaffected. It is "invariant under time reversal", where the operation of time reversal involves reversing the directions of both time and motion. If the operation of time reversal does not leave the process unaffected, i.e. if reversion? motion leads to a result that is different from the result of reversing time, then the process is temporally irreversibility. The test for invariance under time reversal as applied to the equations describing the process can be illustrated as follows.

Consider one particle *or* mass  $m$  moving in the  $x$  direction with velocity  $v$  under a force  $F$ . The Newtonian equation can be listed as

$$m \left( \frac{dv}{dt} \right) = F(x)$$

$$v = \left( \frac{dx}{dt} \right)$$

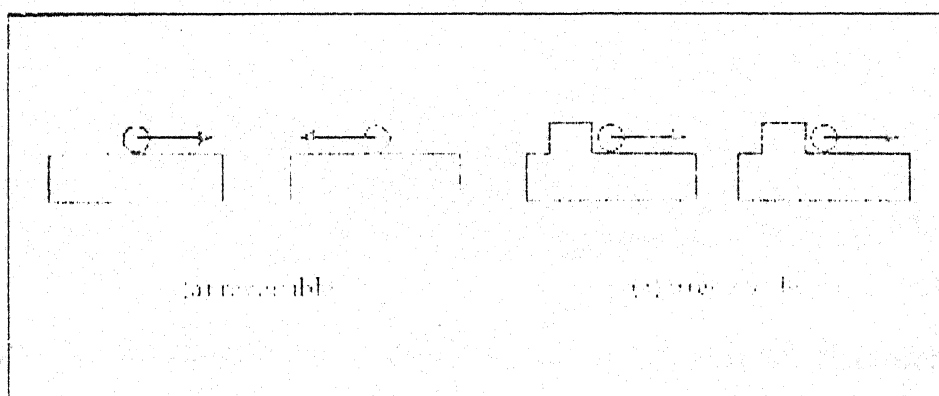
If we reverse the signs of both  $t$  and  $v$ , we leave the equations unchanged, which is to say that they are "invariant under time reversal".



Thus the motion of a particle governed by Newtonian mechanics is temporally reversible. The same can be said for the evolution of any collection of particle described by the Newtonian scheme or any schemes inherited from that including quantum mechanical schemes, relativistic schemes, and probably any future schemes. The present physics of particle collections is temporally reversible in the sense of the following criterion:

**"Temporal reversibility:**

A process is reversible if it can be reversed by reversing the direction of time. The criterion for temporal reversibility (irreversibility) is illustrated by Figure 6. In Figure 6 we see motion to the right converted to motion to the left by reversing the direction of time. The same reversal could have been accomplished by simply reversing the initial velocity of the rolling ball and not carrying out that cosmic miracle of reversing time. In other words, reversing time is the same as reversing motion, and if we



**Fig.6 TEMPORAL REVERSIBILITY AND IRREVERSIBILITY**

reverse both time and motion the result will be the same as if we had not reversed either. If the process were not reversible in this time since then we could have the strange situation pictured in Figure 6(b). Reversing time would lead to result totally unexpected in our memory.

It may be seen obvious at this point that temporal irreversibility is impossible. All processes at all levels of description must be temporally reversible. Otherwise we would have no memories, no sense of time. And yet there is a strong tradition that identifies the "arrow of time" implies by thermodynamic irreversibility with "violations" of temporal reversibility (12) due to a variety of possible causes ranging from the uncertainty principle to cosmological factors involved in the way the universe was formed. And symptoms of temporal irreversibility have been identified; it is generally assumed, for example, that some of the equations for macroscopic processes such as diffusion (13) are not invariant under time reversal. The current argument by readers in the field such as Prigogine (14) is that we have to revise fundamental physics so that it can incorporate temporal irreversibility in order to account for thermodynamic irreversibility. We cannot simply ignore temporal irreversibility as a possible component of thermodynamic irreversibility.

At this point we have three simple kinds of reversibility (irreversibility). We have not found any other simple kinds and so we expect to find that other kinds (thermodynamic, kinetic, electrochemical, etc.) are equals or composites of these' three simple kinds:

### Simple Kinds of Irreversibility

Kind	The process cannot be reversed by
Intertial	changing external conditions
Directional	changing internal conditions
Temporal	changing the direction of time

It is usually clear what is meant by changing external condition. What we mean here by changing internal conditions is changing the directions of the molecules, which would certainly reverse the process. The problem with fluids is that we cannot change the directions of the molecules. This is not to say that there is a conceptual obstacle to one of the other direction, as illustrated in Figure 5(b), but that the collection of molecular directions that can occur naturally is restricted in some way that leaves observed fluids predisposed to go one way and not the other. No such predisposition is anticipated in the life of an individual particle, and we have to wonder where that predisposition comes from into life of a large collection of particles.

### Conclusion:

Thermodynamic irreversibility is a composite of two simple kinds, namely, inertial and directional. It remains to be seen what, if any, relation it has to temporal irreversibility. When it is introduced in terms of the expanding gas, where the process is said to be reversible if it can be

reversed by slight change of the external pressure  $P$ , it is introduced as "inertial" irreversibility. When it is noticed, later on, that a gas expanding against an external fluid at lower pressure generate entropy, " then the process is said to be irreversible in a directional sense. The forward direction is "spontaneous" while the reverse direction is excluded. To cover both cases we have to recognize both criteria. We could say that a process is irreversible if it has (or will soon have) "inertia" and if it has "spontaneity" (is going or will be going in the allowed direction).

Both terms, "inertia" and "spontaneity", are somewhat inadequate. What we mean for fluid processes is that the process has inertia. if it is not at equilibrium and has spontaneity if it is going in the naturally allowed direction. Thus inertia and spontaneity are not quite the same thing, and we should distinguish between them. Thermodynamic irreversibility is a composite of inertial irreversibility (not at equilibrium) and a directional irreversibility that is natural (not conceptual) in origin.

In contrast, "kinetic irreversibility" is not a composite. It is purely "directional" with no inertial component. What is meant by "irreversibility" in chemical kinetics (and related areas) is that the rate coefficient for one or the other direction is negligible. Thus a chemical reaction is kinetically reversible if both directions are significant and this can be the case even if the reacting system is nowhere near equilibrium. The inertial requirement, which is emphasized so frequently in " thermodynamic contexts, is missing in kinetics.

### APPLICATION:

The first chapter of the thesis "THERMODYNAMIC IRRVERSIBILITY" is purely theoretical in which, what and types of irreversible thermodynamics are tried to explain. This process is also known as Non-equilibrium Thermodynamics. All process which are one directional in normal course, can be taken into account for their studies on the basis of "IRREVERSIBLE THERMODYNAMICS". Transport studies of the synthetic and biological membranes are best explained on is' the basis of it. Narebska andKoter(15), in their publication: "Irreversible Thermodynamics of Transport Across charged Membranes" discussed the results for the degree of coupling and efficiency of energy conversion for the system composed of a perfluorinated Nafion 120 membranes and sodium chloride solutions of different concentration. Bogdau Tomicki (16) used the non-equilibrium thermodynamics to explain the mechanism of membrane permeation supplemented with the momentum low in the form of the mechanical equilibrium equation. For the membrane transport system, Yusukemai (5) also took the irreversible thermodynamics into account. The parchment supported membranes, moulded membranes, and some biological (i.e. natural) membranes have also been studied (17-22) for the evaluation of their membrane parameters using the principles of irreversible thermodynamics.

In the thesis the preparation of the synthetic membranes and the studies of their characterization based on the principles of irreversible

thermodynamics are well explained. However, the membrane studies relating to comparisons of their different structure and nature with respect to the membrane selectivity were also carried out successfully by the fully developed theories of thermodynamics of irreversible processes.

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## Chapter-II

# MECHANICS OF MEMBRANE PERMEATION

The study of the mechanical aspects of membrane permeation has been a subject of increasing interest in recent years. The development of the theory of the interaction between the membrane and permeating species makes it possible to use the laws of mechanics alongside those of thermodynamics in the description of membrane permeation. Such an approach has already helped to resolve the long-standing problem

Chapter-II

**MECHANICS OF MEMBRANE  
PERMEATION**

## Chapter -II

# MECHANICS OF MEMBRANE PERMEATION

### **Introduction :**

In 1968 Manning [1] put forth a model of membrane permeation known as the 'energy - barrier model'. For a two component liquid solution permeating a membrane it consists in assuming that the solute is subject to a spatially varying but time-independents external force, which is of potential character and can be expressed as  $V(x) = - dV/dx$ , where  $V(x)$  is a potential energy function. The solvent is not experiencing such a force. Thus the membrane is modelled as a potential energy barrier for solute only. Both solute and solvent interact frictionally with the membrane when they flow. Otherwise the membrane is non-existent, i.e. it occupies no volume.

Subsequently, the energy-barrier model was applied for describing osmosis, imbibition and capillary osmosis (2-4). The allowance for potential interaction between the membrane and permeating species makes it possible to use the laws of mechanics alongside those of thermodynamics in the description of membrane permeation. Such an approach has already helped to resolve the long-standing problem

with the mechanism of osmotic flow and cleared up the role of pressure in it (4).

On the other hand, diffusion of electrolytes across the model membranes (5-12) has been studied using the Fick's Diffusion law and Nernst Planck formulae for Electrical Potential and the Theory of Absolute Reaction rate by evaluating the energetic membrane parameters. Further, membrane transport system modeled by network thermodynamics (13), modified Kedem-Katchalsky equations and their applications (14), extended Nernst-Planck Model (15) etc. have been main contributing theories regarding the well characterisation of both synthetic and biological membranes. Recently, Bogdan Tomicki (16) has presented the physics of electrical effects and every conversion on membranes in the direction of making the membrane system as multidisciplinary field of studies.

The present studies show that when the idea of solute membrane potential interaction is applied, the laws of mechanics can be used consequently in the description of membrane transport. Under the condition that the membrane allows only diffusive flows to occur, the mechanics is very simple and contained in the mechanical

equilibrium equation :  $\bar{v}_P = \sum \bar{c}_i f_i^{ext}$ . This equation was of course used in previous theories. For instance, a paper by Smit et al. (17) combines explicitly the mechanical equilibrium equation with the Gibbs-Duhem equation as we do here. However, it fails to allow the beginning for potential interaction between the membrane and permeating species. Only at the end, as a finishing touch, the potential interaction is allowed for via the partition coefficient, this being common practice in many other theories.

Operating within the energy-barrier model convention we treat here the permeating solution as the thermodynamic system under study, relegating the membrane to the surroundings. Then the membrane solution interaction appears in the description as an external force of both potential and frictional character. Even with equilibrium thermodynamics this approach gives us very readily a very useful and important equation which contains both thermodynamics and mechanics of membrane permeation, the latter coming from the mechanical equilibrium equation.

To obtain an irreversible thermodynamic description of membrane permeation it suffices only to supplement the momentum balance equation, used in the course of the derivation of the dissipation, with external forces of friction

on the permeating components. Then the obtained dissipation function contains an additional term dependent on the centre-of-mass velocity and the external forces of friction. So the function is not invariant under the frame of reference transformation and Prigogine's theorem is not applicable here. What is more, the equation which shows the non-applicability of Prigogine's theorem is just our afore-mentioned important equation.

Relegating the membrane to the surroundings is not free of a restriction. This can only be done when the thermodynamic state of the membrane does not change. During stationary permeation this condition is fulfilled.

The other alternative approach is to treat the membrane as belonging to the system under study. Then all membrane-species interaction forces become internal, and the only external force is on the membrane itself. As this force is non-dissipative, Prigogine's theorem applies and the dissipation function can be easily rewritten with fluxes in the membrane-fixed frame of reference.

As a test of practical usefulness of the proposed approach, the irreversible thermodynamic description is combined here with the frictional model of membrane permeation. On casting the phenomenological equations

into the form of the practical Kedem - Katchalsky equations,<sup>58</sup> it turns out that four practical coefficients are needed in order to determine the three friction coefficients and the partition coefficient.

As only diffusion dissipation is considered and the mechanical equilibrium amply used through out this report, the theory presented here is applicable only for dense enough membranes which do not allow viscous flow to occur. However, an indication is given how this restriction can be lifted and viscous flow allowed for.

## **DISCUSSION**

**Detailed discussion of the mechanics in membrane permeation is presented under the following heads:**

**Equilibrium thermodynamics and mechanics of membrane permeation**

*Permeating solution as the thermodynamic system under study*

In order to obtain a consistent mechanical and thermodynamic description of membrane permeation, we have to supplement the energy balance equations of



equilibrium thermodynamics with a mechanical energy contribution. This is in line with the energy-barrier model which envisaged the membrane just as a potential field  $V(x)$ . Thus the starting equation is the well-known expression for internal energy increment (of small enough volume element) with an additional term  $dE^{ext} d\bar{x}$ , which describes energy changes due to displacement of the system in an external field of potential forces  $\bar{F}^{ext}(x)$  all membrane-solution interactions being counted as external.

$$dE = TdS - pdV - \bar{F}^{ext}(x) d\bar{x} + \sum \mu_i(x) dn_i \quad (1)$$

Consequently, for the Gibbs free energy increment we have

$$dG = Sdt + Vdp - \bar{F}^{ext}(x) d\bar{x} + \sum \mu_i(x) dn_i \quad (2)$$

with  $G(T, p, x, n_i)$  dependent not only on temperature, pressure and composition, but also on space coordinate  $x$ . The position-dependent chemical potential is defined as follows:



$$\left( \frac{\partial G}{\partial n_i} \right)_{p, T, x, n_j = 1} = \mu_i(x) \quad (3)$$

Being a partial quantity the chemical potential satisfies the equation  $G(x) = \sum n_i \mu_i(x)$ . A differential of this when compared with eqn. (2) gives for isothermal conditions the equation:

$$dp = \sum c_i d\mu_i(x) - \bar{f}^{ext,p} d\bar{x} \quad (4)$$

where  $\bar{f}^{ext,p} = F^{ext}/V$  represents volume density of the external potential force. Now eqn.(4) can be combined with the mechanical equilibrium equation.

$$Vp = \sum C_i (\bar{f}_i^{ext,p} + \bar{f}_i^{ext,f}) \quad (5)$$

resulting in

$$\sum C_i (V\mu_i(x) - \bar{f}_i^{ext,f}) = 0 \quad (6)$$

The occurrence of frictional forces,  $\bar{f}_i^{ext,f}$  means of course that we have now departed strict thermodynamic equilibrium, but not far from it so that the relations of

$$\left( \frac{\partial G}{\partial n_i} \right)_{p, T, x, n_j = 1} = \mu_i(x) \quad (3)$$

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resulting in

$$\sum C_i (V\mu_i(x) - \bar{f}_i^{ext, f}) = 0 \quad (6)$$

The occurrence of frictional forces,  $\bar{f}_i^{ext, f}$  means of course that we have now departed strict thermodynamic equilibrium, but not far from it so that the relations of

equilibrium thermodynamics stay valid locally (the condition of local equilibrium as applied in nonequilibrium thermodynamics).

Expressing the position-dependent chemical potential as  $\mu_i(x) = \mu_i^0 + \bar{V}_i p + \mu_i^E$  (definition of  $\mu_i^E$  follows eqn. 7) and assuming that  $V\mu_w^E = 0$  within a homogeneous membrane, we obtain from eqn. (6) for a two component solute-water system the relation : where  $\bar{f}_{sn} = \bar{f}_s^{exl.f} - \bar{V}\mu_s^E$ . The obtained equation says that the force of solute-membrane interaction,  $c_s f_{sn}$ , balances the water-membrane force of friction plus the applied pressure gradient. So this force is the driving force for osmotic volume flow.

Thus eqn. (6) is very important result of the present study. It contains both mechanics and thermodynamics as applied to membrane permeation. Its usefulness for explaining the mechanism of osmotic flow has been shown by Tomicki [4]. The idea of such a description of membrane transport evolved from the energy-barrier model first proposed by Manning [1]. The present chapter shows that the energy-barrier model is no longer a model but simply a result of applying the laws of mechanics and thermodynamics to membrane transport.

We can also construct a thermodynamic description of our system leaving aside the mechanical energy. The expression for internal energy changes is now without the term  $F(\mathbf{x}) d\mathbf{x}$ , and the chemical potential does not depend explicitly on space coordinate. It is the normal chemical potential  $\mu_i$  as used in the thermodynamics of free solutions, which satisfies the Gibbs-Duhem equation:  $dp = \sum c_i d\mu_i$ . In thermodynamic equilibrium the mechanical equilibrium condition requires that  $\bar{V}_P = \sum c_i \bar{f}_i^{ext.P}$ . Combining this with the Gibbs-Duhem equation, we get

$$\sum C_i (\bar{V} \mu_i - \bar{f}_i^{ext.P}) = 0 \quad (7)$$

Since the external forces are arbitrary and the concentrations are positive numbers, the last equation requires that  $\bar{V} \mu_i - \bar{f}_i^{ext.P} = 0$  for each component. Now we put  $\bar{f}_i^{ext.P} = -\bar{V} \mu_i^E$  by definition, thus defining an excess of chemical potential which is due to the external potential force. The equation before the last can now be rewritten as  $\bar{V} \mu_i(x) = 0$ , with  $\mu_i + \mu_i^E$  being the so called augmented chemical potential.

As in thermodynamic equilibrium  $\bar{V}p = \sum c_i \bar{f}_i^{\text{ext},p} = \bar{f}^{\text{ext},p}$  eqn. (4) can be reduced to  $\sum c_i \bar{V} \mu_i(x) = 0$ , the same as eqn. (7).

We now identify the position-dependent chemical potential of eqn. (4) with the above defined augmented chemical potential. After this, eqn. (4) is seen to be easily reducible to the Gibbs - Duhem equation

$$\bar{V}p = \sum c_i \bar{V} \mu_i \text{ or } \sum c_i \bar{V} \mu_i^0 = 0 \quad \mu_i = \mu_i^0 + \bar{v}_{ip} + \mu_i^c$$

### **With membrane belonging to the system under study**

The other alternative approach to membrane transport is to regard the membrane as an integral part of the system under study. We thus have an n-component mixture (the n<sup>th</sup> component being the membrane) with an external force on the membrane only. As it is a mechanical force, we can construct the equilibrium thermodynamics of our system without taking it into account. The external potential forces on the permeating solution now become internal membrane-species interactions. Such interactions are of course coeternal membrane-species interactions. Such interaction is of course contained in the usual chemical potential of the species. However, we have to keep in mind that the potential here is position-dependent besides being concentration,

temperature and pressure dependent as is the case in thermodynamics of free solution. Thus we can write :

$$dG = - SdT + Vdp + \sum^n \mu_i(x) dn_i, \quad (8a)$$

$$G = \sum^n \mu_i(x) n_i, \quad (8b)$$

The two equations when combined give us the Gibbs-Duhem equation :  $\bar{V}p = \sum^n c_i \bar{V} \mu_i(x)$ . Now if chemical potentials of all the components could be expressed as

$$\mu_i(x) = \mu_i^o + \bar{V}_i p + \mu_i^E(x) + \mu_i^c, \quad (9)$$

the following relation would result from the Gibbs-Duhem equation :

$$\sum^n c_i d\mu_i^E(x) + \sum^n c_i d\mu_i^c = 0 \quad (10)$$

However, we cannot do it like that because the  $n^{\text{th}}$  component of the system, the membrane, differs in that it is a solid phase whose chemical potential can not be expressed by formula (9). The chemical potential of the membrane does not depend on pressure because a membrane equilibrated with a solution does not participate in the overall pressure, i.e. its partial pressure is zero. Also the membrane potential does not depend on concentration, as its concentration gradient is maintained by the forces of cohesion that keep the solid phase together. Thus, for the

membrane we may write :  $\mu_n = \mu_n^0 + \mu_n^E$  In spite of that we can, however, show that eqn. (10) holds for membrane permeation. In order to do that, we have to camouflage the solid component of our mixture by lumping it with one of the volatile components, i.e. a component whose chemical potential can be related to the Gibbs free energy of a gas or to saturated vapour pressure by Raoult's law. If we choose this component to be water, then we can operate with a water-membrane chemical potential  $\mu_{wm}$  and the Gibbs-Duhem equation can be written as

$$dp = c_{wn} d\mu_{wn}(x) + \sum^{n-2} c_i d\mu_i(x) \quad (11)$$

Comparing this with the normal form of the Gibbs-Duhem equation, we get

$$c_{wn} d\mu_{wn} = c_w d\mu_w + c_n d\mu_n \quad (12)$$

With now having all components in eqn. (11) volatile we can use expression (9) for their chemical potentials and rewrite eqn. (11) as follows :

$$c_{wn} d\mu_{wn}^E + \sum^{n-2} c_i d\mu_i^E + c_{wm} d\mu_{wn}^c + \sum^{n-2} c_i d\mu_i^c = 0 \quad (13)$$

Expression (9) and eqn. (12) imply the following equalities :

$$c_{wn} \bar{V}_{wn} = c_w \bar{V}_w = c_n \bar{V}_n \quad (14a)$$

$$c_{wn} d\mu_{wn}^E(x) c_w d\mu_w^E(x) = c_n d\mu_n^E(x) \quad (14b)$$

$$c_{wn} d\mu_{wn}^c(x) c_w d\mu_w^c(x) = c_n d\mu_n^c(x) \quad (14c)$$

These may be regarded as defining the respective components of  $\mu_{wn}(x)$ . Using eqns. (14) we see that eqn. (10) results, but in the second term of the equation the summation is over  $n-1$  species because by the above given argument about chemical potential of the membrane. Now,  $\sum^n c_i d\mu_i^c = 0$  as we have seen at the end of the last section. So the first term in eqn. (10) also must be zero and thus we have:

$$\sum^n c_i V \mu_i^E(x) = 0 \quad (15a)$$

$$\sum^{n-1} c_i V \mu_i^c = 0 \quad (15b)$$

The two equations express the nontrivial content of the Gibbs-Duhem equation in membrane transport.

Although expressed in terms of forces, eqns. (15a & 15b) do not contain the momentum conservation law; the forces appear simply by way of dividing the energy equation by  $dx$ . The momentum conservation law provides another independent equation in the form of the mechanical equilibrium equation. This equation when combined with the Gibbs-Duhem equation gives us



$$\sum^n c_i \bar{V} \mu_i(x) - \sum^n c_i \bar{f}_i^{ext} = 0 \quad (16)$$

In the case of membrane permeation the sum of external forces reduces to  $c_n \bar{f}_n^{ext}$  ( $\bar{f}_{i \neq n}^{ext} = 0$ ) since only the membrane is kept fixed in the laboratory by external forces. That force is transmitted totally to the permeating solution. Thus we can write :

$$\sum^n c_i \bar{f}_i^{ext} = c_n \bar{f}_n^{ext} = \sum c_i (\bar{f}_{in}^f + \bar{f}_{in}^p) \quad (17)$$

The forces in the last term of eqn. (17) represent frictional and potential interactions, respectively between the membrane and permeating species, and the summation runs from 1 to (n-1), i.e. over all components of the permeating solution. (Any summation sign without superscript in this paper means just that.) It should be stressed here that the two equality signs in eqn. (17) hold under the following two conditions : (a) external interaction is transmitted only via the membrane (first equality), and (b) the membrane is a solid phase, i.e. its partial pressure is zero (second equality).

Using eqn. (17) we can now rewrite eqn. (16) as follows:

$$\sum^n c_i \bar{V} \mu_i(x) - \sum c_i (\bar{f}_{in}^f + \bar{f}_{in}^p) = 0 \quad (18a)$$

$$\sum c_i (\bar{V} \mu_i(x) - \bar{f}_{in}^f) + c_n \bar{V} \mu_n(x) - \sum c_i \bar{f}_{in}^p = 0 \quad (18b)$$

As by definition  $\bar{f}_{in}^p = -\bar{V} \mu_i^E(x)$  and  $\bar{V} \mu(x) = \bar{V} \mu_n^E$ , with the use of eqns. (15) we have

$$c_n \bar{V} \mu_n(x) \sum c_i \bar{f}_{in}^p = \sum^n c_i \bar{V} \mu_i^E = 0 \quad (19)$$

Thus, finally, on identifying  $f_{in}^f$  with  $f_i^{ext.f}$  with of the first section, from eqn. (18b) we get

$$\sum c_i (\bar{V} \mu_i(x) - \bar{f}_i^{ext.f}) = 0 \quad (20)$$

This is again the basic equation of the energy barrier mode [4]. From the way it is derived here one can see that it contains none of the restrictions that a model might impose. No special assumptions were made. The two conditions (a) and (b) involved in eqn. (17) are simple facts of membrane permeation and thus imply no restrictions.

The concentrations in eqn. (20) refer to unit volume of geometrical space, not to unit volume of the permeating solution as is the case in eqn. (6). Within a membrane the two concentrations are of course not the same, but related to each other as follows :  $c_i = C_i (1 - O_m)$  where  $C_i$  is the concentration of eqn. (20),  $c_i$  that of eqn. (6), and  $O_m$  the volume fraction occupied by the membrane. However, multiplication by a constant  $(1 - O_m)$  has no meaning in eqn. (20), and thus the two equations are identical.

Besides providing another independent derivation of eqn. (6), this section shows us also that the mechanics and thermodynamics of a system do not depend on the way of description; whether the membrane forms a part of the system and with an external force on the membrane or is relegated to the surroundings, thereby giving the membrane - solution interactions the status of external forces, is irrelevant for the mechanics of the system. Once the presence of a membrane is accounted for in the chemical potential of the solution components are related to a geometrical unit of space or to a unit of the solution volume. On deeper reflection we see that this must be so, for otherwise the thermodynamics of a solution would depend on the shape of the vessel containing the solution.

### **Irreversible thermodynamics for membrane permeation**

*Permeating solution as the thermodynamic system under study-with allowance for viscous flow*

Irreversible thermodynamics of membrane permeation, like equilibrium thermodynamics, can be constructed using either the energy-barrier model convention or without it. In the first case the described system is a solution (without membrane) which is acted upon by external forces of both frictional and potential character. In the latter case the

membrane forms as integral part of the system and there are no external forces of friction.

To obtain the irreversible thermodynamics of membrane permeation in the first case it suffices only to modify the usual thermodynamics of free solution by supplementing the momentum balance equation with external forces of friction. The equation then has the form

$$\rho \frac{d\bar{v}}{dt} = - \text{Div } II + \sum c_i (\bar{f}_i^{\text{ext},p} + \bar{f}_i^{\text{ext},f}) \quad (21)$$

where  $p$  is the density of the solution  $v$ , its centre of - mass velocity.  $II$  the pressure tensor,  $c_i$  the concentration of the  $i$ th species, and  $\bar{f}_i^{\text{ext},p}$  and  $\bar{f}_i^{\text{ext},f}$  the external forces per mole of it species of potential and frictional character, respectively. Now, proceeding according to text-books e.g [18] we obtain the following expression for the isothermal dissipation function:

$$\sigma T = \sum c_i (\bar{v}_i - \bar{v}) (\bar{f}_i^{\text{ext},p} - \bar{V} \mu_i) - \bar{v} \sum c_i \bar{f}_i^{\text{ext},f} \quad (22)$$

On applying (6) expression (22) transforms to

$$\sigma T = - \sum \bar{I}_i^n \bar{V} \mu_i (x) \quad (23)$$

Thus in the membrane-fixed frame of reference the dissipation function has the simple form which results from

the so-called discontinuous approach. It can also be concluded here that the mechanics of membrane permeation stay the same no matter whether equilibrium or irreversible thermodynamics is applied.

As in general, according to eqn. (6)  $\sum_i \bar{V}_i \mu_i(x) \neq 0$ , the dissipation function is not invariant under transformation to another frame of reference meaning that Prigogine's theorem is not applicable here. The whole membrane system can, of course, be moved in the laboratory with arbitrary  $v_a = v_n$  but the diffusion fluxes must still be measured relative to the membrane if dissipation is to stay the same:

$$\sigma T = - \sum (\bar{I}_i^n + \bar{v}_n - \bar{v}_n) \bar{V}_i \mu_i = - \sum \bar{I}_i^n \bar{V}_i \mu_i(x) \quad (24)$$

At this point it should be added that Prigogine's theorem does apply when the membrane belongs to the described system. Then the dissipation function has the form of eqn. (32) and in view of the first equality (35) the diffusion fluxes can be measured in any moving frame of reference we choose. This means that the membrane system in the laboratory can be moved at will without changing the dissipation which occurs within the system. Such a property is clearly obvious as far as the external force on the

membrane,  $f_n^{ext}$ , is not dissipative. However, in any reference frame we choose we are not allowed to put  $v_n$  or any other species velocity equal to zero. By doing so we separate the system into two parts; one moving and one stationary. Unless the two parts interact frictionally between each other, the dissipation is of course dependent on relative velocity between them, as eqn. (22) indicates. Putting  $v_n=0$ , we see the dissipation function (32) transforming to eqn. (22) as follows :

$$\begin{aligned}\sigma T &= -\sum^n \bar{I}_i^c (\bar{V} \mu_i(x) - \bar{f}_i^{ext}) = -\sum \bar{I}_i^c \bar{V} \mu_i(x) - \bar{f}_n^{ext} \\ &= -\sum \bar{I}_i^c \bar{V} \mu_i(x) + \bar{v} c_n (V \mu_n(x) - f_n^{ext})\end{aligned}\quad (25)$$

As the external force is transferred onto the permeating species in two forms. we can put  $c_n f_n^{ext} = c_n f_n^{ext,p} + c_n f_n^{ext,f} + \sum c_i f_{in}^f$ . Using this and eqn. (15a), we obtain the dissipation function in the form of eqn. (22), for which Priogine's theorem does not apply.

By using relations (20) and (4) we have

$$\sum c_i \bar{f}_{in}^f = \sum c_i \bar{V} \mu_i(x) = \bar{V} p - \bar{f}^{ext,p}\quad (26)$$

With eqn. (26) eqn. (22) can be rewritten as follows:

$$\sigma T = \sum \bar{I}_i^c \bar{V} \mu_i(x) - \bar{v} (\bar{V} p - \bar{f}^{ext,p})\quad (27)$$

The phenomenological equations can be constructed by using either dissipation function in the form of eqn. (27) or eqn. (23). Thus on the basis of eqn. (27) we can write

$$\bar{I}_i^c = - \sum \bar{I}_{ij}^c \bar{V} \mu_j (x) \text{ and } \bar{v} = - L_p^d (\bar{V} p - \bar{f}^{exl.p}) \quad (28)$$

Consequently, the fluxes relative to the membrane can be obtained as follows:-

$$\bar{I}_i^n = \bar{I}_i^c + c_i \bar{v} = \sum L_{ij}^c \bar{X}_j + c_i L_p^d (\bar{f}^{exl.p} - \bar{V} p) \quad (29)$$

Alternatively, using expression (23) we have

$$\bar{I}_i^n = \sum L_{ij}^n \bar{X}_j \quad (30)$$

Comparing eqn. (29) with eqn. (30) and using eqn. (26) we get

$$L_{ij}^n = L_{ij}^c + c_i c_j L_p^d \quad (31)$$

The centre-of-mass velocity  $v$  used so far was due to diffusion only. If viscous flow occurs within a membrane, the centre of mass can move due to viscous flow independently of the diffusive flow. So we can write  $\bar{v} = \bar{v}_d + \bar{v}_v$ , where  $v_d$  and  $V_v$  are diffusive and viscous contributions, respectively; and the fluxes relative to the membrane are  $\bar{I}_i^n = \bar{I}_i^c + c_i (\bar{v}_d + \bar{v}_v)$ . Now the treatment of viscous flow given by Mason and Castillo (19) can be followed, with some



modification coming primarily from the fact that the authors have omitted the diffusive centre-of-mass velocity  $u_d$ .

#### 4. Irreversible thermodynamics combined with the frictional model

Treating the membrane and permeating solution as a system which does not interact frictionally with the surroundings, we can write the dissipation function as follows :

$$\sigma T = - \sum^n c_i (\bar{v}_i - \bar{v}) (\bar{V} \mu_i(x) - \bar{f}_i^{ext}) = \sum^n \bar{I}_i^c \bar{X}_i \quad (32)$$

where  $\bar{f}_{i \neq n}^{ext} = 0$  is the total external nondissipative force which keeps the membrane in fixed position in the laboratory. The corresponding phenomenological equations are :

$$\bar{I}_i^c = \sum^n L_{ij}^c \bar{X}_j, \quad \bar{X}_i = \sum^n R_{ij}^c \bar{I}_j^c \quad (33)$$

Now the so-called statistical-mechanical theory (20-22) gives us equations which can be called either Stefan-Maxwell equations, Bearman-Kirkwood equations, or Spiegler frictional equations:

$$\bar{X}_i = \sum^n \frac{RT_{cj}}{cD_{ij}} (\bar{v}_i^c - \bar{v}_j^c) = \sum^n f_{ij} (\bar{v}_i - \bar{v}_j) \quad (34)$$



where  $D_{ij}$  = description of the interdiffusion of species  $i$  and  $j$ ,  
 and  $\bar{v}_i^E = I_i^c / c_i$ ,  $c = \sum^n c_i$ , and  $\bar{v}_i$  are velocities in the  
 membrane - fixed frame of reference, and  $f_{ij}$  are friction  
 coefficients exchangeable with partial friction coefficients  
 $\xi_{ij} = f_{ij} / c_j$ .

Equations (34) when multiplied by  $c_i$  and added up,  
 give us the equations:

$$\sum^N c_i \bar{X}_i = 0, \quad (35a)$$

$$\sum^{n-1} c_i (\bar{V} \mu_i(x) - \bar{f}_{in}^f) = 0 \quad (36b)$$

where  $\bar{f}_{in}^f = -v_i f_{in}$  is the force of friction between the  
 membrane and each of the permeating species. Thus friction  
 consideration of the frictional model provides us with yet  
 another independent derivation of our basic equation (6).

The two eqns. (35) together with eqn. (4) allow us to  
 find that

$$\bar{X}_n = \bar{f}_n^{ext.f} = (\bar{V} p - c_n \bar{f}_n^{ext.p}) / c_n \quad (36)$$

Equations (34) can be easily rewritten in the form of the  
 resistance representation of the phenomenological  
 equations, thus offering correlations between resistance

coefficients  $R_{ij}^c$  and friction coefficients  $\hat{I}_{ij}$ . Using eqn. (35a) we can reduce the number of frictional as well as phenomenological equations to  $(n-1)$ , where the summation runs over all permeating species only and the fluxes are those in the membrane fixed frame of reference.

The same result can also be obtained by starting with application of Prigogine's theorem to the dissipation function by putting  $v=v_n=0$ . The function then reduces to  $\sigma T = \sum \bar{I}_i'' \bar{X}_i$ , where  $\bar{I}_i''$  are fluxes measured relative to the membrane and  $\bar{X}_i \bar{V} \mu_i(x)$ . Now the frictional equations allow us to write  $n$  equations with  $n$  forces and  $(n-1)$  fluxes. However, the number of equations can be reduced by using eqn. (35a). Thus again the frictional equations can be brought to the same form as the phenomenological equations resulting from the reduced form of the dissipation function.

There is a third way of handling, consisting in that we first reduce the number of fluxes by using the relation  $\sum^n \bar{I}_i^c = 0$ . Then in order to show a complete correspondence between the frictional equations and phenomenological ones we have to use eqn. (35b).

The remaining task is to express the frictional coefficients by the practical phenomenological coefficients in order to determine the former from measurements of the latter. To this end we have to integrate the frictional equations over the membrane thickness. For a binary solution the equations have the form:

$$-V\mu_s(x) = (f_{sw} + f_{sn}) \bar{v}_s - f_{sw} \bar{v}_w \quad (37a)$$

$$-V\mu_s(x) = -f_{ws} \bar{v} + (f_{ws} + f_{wn}) \bar{v}_w \quad (37b)$$

Integrating the left-hand side we have

$$\int_0^d \mu_s(x) dx = c_s \bar{V}_s \Delta p + \int_0^d c_s d\mu_s^E + \Delta\pi = \phi_s \Delta p + K\Delta\pi \quad (38)$$

To perform the integration on the right-hand side of eqn. (38) we assume that at the solute-membrane physical interface the solute satisfies the Boltzmann equilibrium distribution. Then we find the  $\Delta\pi$  (K-1) is the result of the integration where K is the partition coefficient. With water:

$$\int_0^d c_w \bar{V}_w \mu_w(x) dx = c_w \bar{V}_w \Delta p + \int_0^d c_w d\mu_w^E + \Delta\pi = \phi_w \Delta p + \Delta\pi \quad (39)$$

where  $\mu_w^E$  has been assumed constant within a homogeneous membrane.

As the right-hand sides of eqns. (37) (on multiplying by  $c_s$  and  $c_w$ , respectively) are functions of products and ratios of concentrations, we refrain from integrating them precisely. Instead, we multiply them by the membrane thickness  $d$  and say that all concentrations there are mean values which refer to the whole membrane. In place of the finite difference in expressions (38) and (39) we substitute mean gradients defined by  $\bar{V}p = \Delta p/d$  and  $\bar{V}\pi = \Delta\pi/d$ . The equations thus modified are assumed to be approximately valid for very thin membranes. From those equations we find that:

$$I_s = a\bar{V} = b\bar{V}\pi \quad (40)$$

$$I_w + c\bar{V}p + b\bar{V}\pi \quad (41)$$

where  $a, b, c, d$ , are coefficients dependent on the friction coefficients, concentrations,  $O_s$ ,  $\phi_w$  and  $K$ . Now volume flow can be found

$$\bar{I}_N = \bar{I}_s \bar{V}_s + \bar{I}_w \bar{V}_w = L_{pv} (\sigma \bar{V}\pi - \bar{V}p) \quad (42)$$

$$L_{pv} = \frac{2c_s \bar{V}_s \bar{V}_s f_{sw} + c_s \bar{V}_s^2 f_w + c_w \bar{V}_w^2 f_s}{f_s f_w - f_{sw} f_{ws}} \quad (43)$$

$$\sigma = \frac{\phi_s f_{sw} + \phi_w f_s - Kc_w (\bar{V}_s f_w + \phi_w f_{ws} / c_s)}{2\phi_s \phi_s f_{sw} + \phi_s \bar{V}_s c_w f_w + \phi_w^2 f_s} \quad (44)$$

and  $f_s = f_{sw} + f_{sn} f_w = f_{ws} + f_{wn}$  Combining eqns. (40) and (42)

we obtain

$$I_s = aI_v / L_p + (a\sigma + b) \nabla \pi = \bar{c}_s (1 - \sigma) I_v - \omega \bar{V} \pi \quad (45)$$

where

$$\bar{c}_s = \frac{\bar{V}_w f_{sw}}{2\bar{V}_s \bar{V}_w + \bar{V}_s^2 f_w + \bar{V}_w^2 f_s / c_s} \quad (46)$$

$$\sigma' = \frac{\bar{V}_w f_{sw}}{\bar{V}_s f_{ws} + f_{wn}} \quad (47)$$

$$\omega = \frac{K}{f_s} \left( 1 + \frac{f_{ws} f_{sw}}{f_s f_w} \right) \quad (48)$$

From eqns. (45) and (42) we find that

$$\bar{c}_s (1 - \sigma') L_{pv} = \left( -\frac{I_s}{\Delta p} \right)_{\Delta \pi = 0} = L_{ps} \quad (49)$$

The last equation defines a fourth practical coefficient

$f_{sw}$ ,  $f_{sn}$ ,  $f_{wn}$  needed to find the three friction coefficient and the partition coefficient K. The four relation between the two sets of coefficient are eqns. (43). (44). (48) and (49).

### Conclusions

The unified and consistent theory of membrane permeation achieved in this report is due to the fact that the

thermodynamic description has been supplemented with the momentum conservation law. This law was applied in the form of the mechanical equilibrium equation, which is an equation that results from the momentum balance equation, which is an equation that results from the momentum balance equation on dropping acceleration and viscous terms. This equation had to be added as extra only in the description with the frame of equilibrium thermodynamics, as in irreversible thermodynamics the momentum balance equation has been taken into account in the derivation of the dissipation function. However, it was possible to take full advantage to the momentum conservation law only after making allowance for all the force operating within and on the described system. The lacking force was the potential membrane-species interaction, accounted for here by the excess new the chemical potential.

An important result of the proposed approach is the equation which contribute both thermodynamics and mechanics of membrane permeation (eqn. 6) This equation is indispensable when one asks about the mechanism of osmotic pressure and also about the phenomena where external forces are present, such as imbibition, surface

tension, capillary rise, etc. The equation was derived here in a number of different and independent ways-both from equilibrium and irreversible thermodynamics, and with membrane included or not included in the system.

Another more practical result evolved on combining the irreversible thermodynamic description with the frictional model of membrane permeation. It turns out that four practical phenomenological coefficients ( $L_{PV} = L_P$ ,  $L_{PS}$ ,  $a$ ,  $w$ ) are needed in order to calculate the three friction coefficients ( $F_{SVS}$ ,  $f_{SN}$ ,  $f_{WN}$ ) and the partition coefficient  $K$ . In the Kedem-Katchalsky (23) and Spiegler (22) treatment three practical of  $K$  in order to determine the three friction coefficients. In view of the fact that the measured flux of a per meant is proportional to its mobility and concentrtaion within the membrane, it seems reasonable that measurements of the fluxes should determine not only mobilities (friction coefficients) but also concentrations within the membrane (partition coefficients). The obtained non-equality of the reflection coefficients for osmosis and ultra filtration should also be mentioned, as it is still a problem in the literature, e.g. (24)



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Chapter-III

**METAL ION SELECTIVITY OF  
MEMBRANES**

### Chapter -III

## INTRODUCTION

Recent studies on permeability, fixed charge density and selectivity of various inorganic precipitate membranes have provided reasonably clear picture of the functioning of these membranes in contact with simple electrolyte solutions.

When two electrolytic solutions having different concentrations are separated by a membrane, the mobile species penetrate the membrane and various transport phenomena are induced in the system [1]. The total electric potential difference observed under zero current flow between two aqueous solutions separated by a membrane has been one of the most widely characterized electrochemical and bioelectric phenomena [2-8]. The fixed charge concept of Teorell [9] and Meyer and Sievers [10] for the charged membranes is a pertinent starting point for the investigation of actual mechanisms of ionic or molecular processes which occur in the membrane phase. For biological membranes the electrical potential differences is usually described in terms of Goldman - HodgkinKatz [11-12] equation whereas for certain ion exchange membranes permeable solely to species of one sign, it is described by generalized Nernst equation. Both the Goldman-Hodgkin- Katz and Nernst equations contain ionic permeability ratio terms. Depending on the transport mechanism, or the assumptions made in the derivations, the permeability ratio has been given various physical meanings as : mobility ratio [13], ion exchange equilibrium constant [14], the product of the mobility ratio and the Donnan ratio [9, 10], the product of the mobility ratio and the distribution coefficient ratio [12], the product of the mobility ratio and ion exchange

equilibrium constant [15,16] or the product of the equivalent conductance ratio and the ratio of partition coefficient [2]. Sandblom et al. [2,3,17] have discussed the significance and implications of the observed permeability ratio. Recently a number of reviews have been appeared dealing with the ion selectivity of membranes [18,19-25].

In this chapter the author has confined the work upto the study of the selectivity of metal ions of both the nickel and cobalt phosphate membranes. In order to evaluate the selectivity values of the metal ions in the membrane phase, the measurements of electrical membranes potential, biionic and multi-ionic potential have experimentally been carried out, values of membrane conductance also contribute in these results. Different methods with individual membrane theories based on the principles of non-equilibrium thermodynamics have been used for the evaluation of thermodynamically effective fixed charge density, permeability ratio of cations using conductivity measurements and potentiometric selectivity constant of the parchment supported nickel and cobalt phosphate membranes using experimentally observed values to confirm the findings.

The theory of absolute reaction rates has also been utilized for the evaluation of Arrhenius activation energy ( $E_a$ ), the change of enthalpy ( $\Delta H^*$ ), entropy ( $\Delta S^*$ ) and free energy ( $\Delta F^*$ ) of activation by making use of conductance data observed for membrane in contact with various monovalent electrolytes. On the basis of the magnitude of these thermodynamic activation parameters, the selective membrane behaviour has also been discussed in the light of an advanced theory of membrane selectivity [26].

Parchment supported membranes of nickel and cobalt phosphate respectively were prepared by the method of interaction suggested by Kushwaha et al. [4] with the help of nickel (II) chloride, cobalt (II) chloride, trisodium orthophosphate and parchment paper.

Actually the precipitate formation of nickel and cobalt phosphate takes place in the interstices of the parchment paper by the method of interaction. Thus parchment paper and inorganic precipitate as a whole act as a membrane. The membranes thus prepared were washed with deionized water to remove free electrolytes.

The biionic and multiionic potentials across freshly prepared parchment supported nickel and cobalt phosphate membranes were measured by constructing an electrochemical cell of the following type and using a Pyeprecision vernier potentiometer

Reference electrode	Electrolyte Solution (I)	Membrane	Electrolyte Solution (II)	Reference electrode
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The reference electrodes used were reversible saturated calomel electrode ( $\text{Hg} / \text{H}_2\text{Cl}_2$ ) connected to the solutions via KCl-agar bridges. Membrane potentials were measured by maintaining a tenfold difference in the electrolyte concentrations. The biionic potential (BIP)

measurements were carried out either by keeping the concentration of both the electrolytes same on the two sides of the membrane, or by maintaining the concentration of one of the electrolytes constant and changing that of the other. Multiionic potentials were measured on the lines suggested by Lakshminarayanaiah [27].

For the measurement of electrical conductivity, membrane was first dipped and equilibrated in an appropriate electrolyte solution. It was then clamped between two half cells and measurements were made according to Fig. 1, using a conductivity bridge (Cambridge Instrument Co. Ltd., England). All measurements were carried out at  $25 \pm 0.1$  °C. The error in measurements of membrane potentials was within  $\pm 0.1\%$  whereas electrical conductivity could be measured to better than 0.05%.

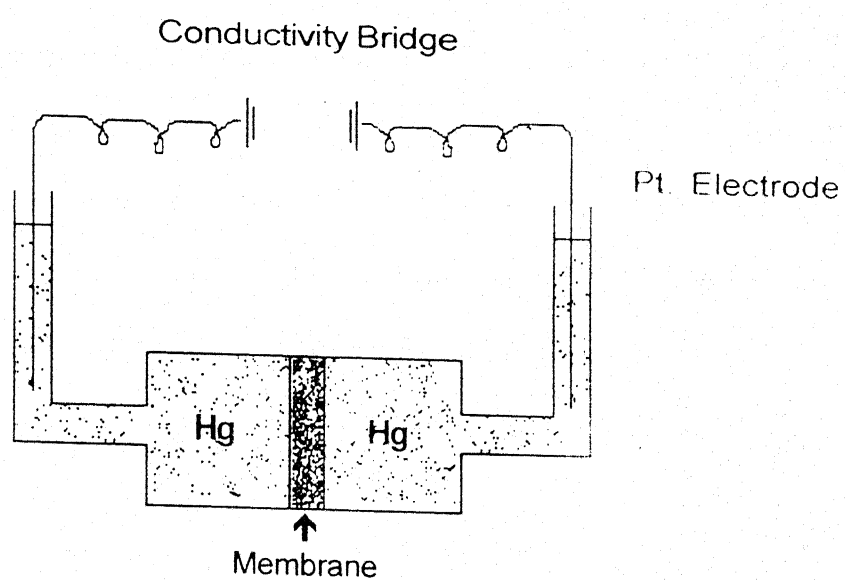


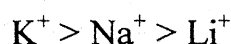
Fig. 1

Cell for measuring the electrical  
conductivity of membrane.



## RESULTS AND DISCUSSION

The values of membrane potential observed experimentally across both the inorganic precipitate parchment supported nickel and cobalt phosphate membrane by taking dilute solution side positive are given in Tables 1 and 2 respectively. The variation of membrane potential with the change of electrolyte concentrations for various 1: 1 electrolytes is shown in Figs. 2 and 3. In both the figures it has been found that membrane potential values decrease with the increase of electrolyte concentration and thus on the basis of these potential values, membranes follow the sequence of the selectivity of metal ions:



In the absence of pressure or temperature gradient, the generation of a steady e.m.f between two solutions of an electrolyte of different concentrations separated by a membrane, can be attributed to the presence of net charge on the membranes. Such charges play an important role in the sorption and transport of simple electrolytes in artificial as well as natural membranes [28 - 30] and impart some important electrochemical properties of coions, counter ions and neutral molecules. Hence, for detailed investigation of membrane selectivity, its thermodynamically effective fixed charge density is to be determined. It

Table 1

The values of the observed membrane potential  $E_m$  (mV) across nickel phosphate membrane at  $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration / Mol $l^{-1}$ $C_{II}/C_I$	KCl	NaCl	LiCl
$1 \times 10^{-1} / 1 \times 10^{-2}$	-42.4	-40.4	-40.5
$5 \times 10^{-2} / 5 \times 10^{-3}$	-40.3	-40.3	-38.0
$1 \times 10^{-2} / 1 \times 10^{-3}$	-32.0	-24.5	-21.5
$5 \times 10^{-3} / 5 \times 10^{-4}$	-15.0	-13.0	-6.9
$1 \times 10^{-3} / 1 \times 10^{-4}$	1.5	9.0	4.5
$5 \times 10^{-4} / 5 \times 10^{-5}$	10.3	10.3	8.0
$1 \times 10^{-4} / 1 \times 10^{-5}$	12.5	12.5	15.3

Table 2

The values of the observed membrane potential  $E_m$  (mV) across cobalt phosphate membrane at  $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration/Mol $l^{-1}$ $C_{II}/C_I$	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	-37.3	-38.7	-35.0
$5 \times 10^{-2}/5 \times 10^{-3}$	-31.4	-36.8	-32.6
$1 \times 10^{-2}/1 \times 10^{-3}$	-28.5	-21.7	-16.4
$5 \times 10^{-3}/5 \times 10^{-4}$	-10.5	-14.5	-10.4
$1 \times 10^{-3}/1 \times 10^{-4}$	1.5	-5.0	5.0
$5 \times 10^{-4}/5 \times 10^{-5}$	9.0	10.0	15.5
$1 \times 10^{-4}/1 \times 10^{-5}$	10.0	15.0	20.0

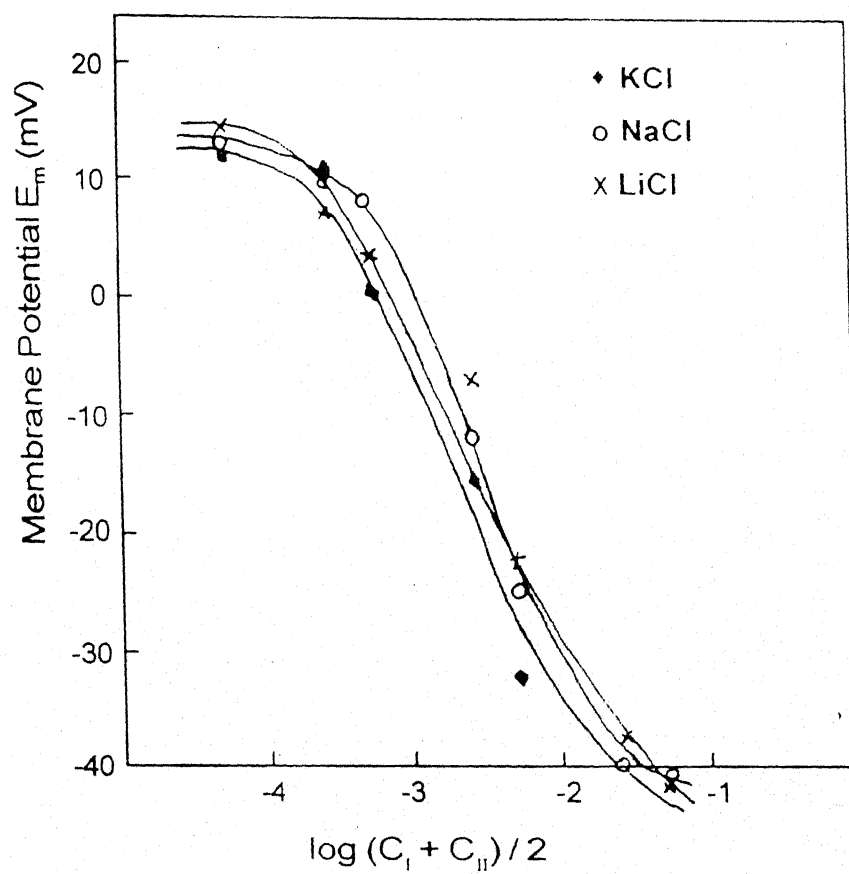


Fig. 2

Plots of membrane potential  $E_m$  (mV) against  $\log (C_I + C_{II})/2$  using 1:1 electrolytes across nickel phosphate membrane.

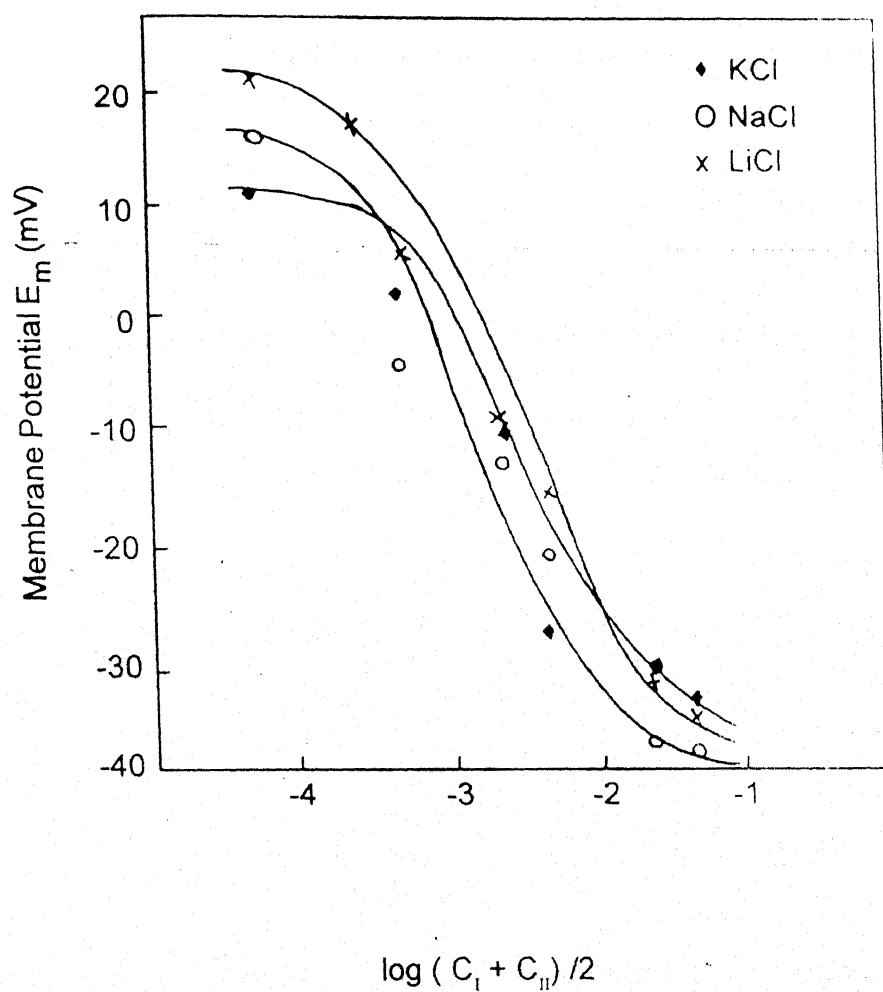


Fig. 3

Plots of membrane potential  $E_m$  (mV) against  $\log (C_I + C_{II}) / 2$  using 1:1 electrolytes across cobalt phosphate membrane

can be evaluated by making the use of an equation derived on the basis of thermodynamics of irreversible processes. This approach employs a phenomenological coefficient to correlate the gradients that exist across a membrane and their resulting fluxes.

Kobatake and coworkers [31,32] integrated basic flow equations, provided by thermodynamics of irreversible processes.. to derive the following equation for the degree of permselectivity ( $P_s$ ) of the membrane electrolyte system by taking into consideration an ionizable membrane in contact with solutions of monovalent electrolyte of concentrations  $C_I$  and

$$C_{II} \text{ ( } C_{II} > C_I \text{ )}.$$

$$P_s = \frac{1 - t_{app} - \alpha}{\alpha - (2\alpha - 1)(1 - t_{app})} = \frac{1}{(4\xi^2 + 1)^{1/2}} \quad (1)$$

where  $\alpha\xi$  and  $t_{app}$  are membrane parameter, i.e., fraction of ionic mobility ratio, relative concentration and the apparent transference number of co ions in membrane phase. Further, these can be expressed as:

$$\alpha = U_+^0 / (U_+^0 + U_-^0) \quad (2)$$

where  $u$  is mobility of ionic species.

$$\xi = C / \phi x \quad (3)$$

$$E_m = - (RT / F) (1 - 2 t_{app}) \ln C_{II} / C_I \quad (4)$$

When the average external salt concentration,  $C = (C_l + C_{||}) / 2$ , is high in comparison with the thermodynamically effective fixed charge density,  $\phi X$ , i.e.,  $\xi \gg 1$ , the membrane potential can be expressed as

$$E_m = - (RT / F) (2\alpha - 1) \ln C_{||} / C_l \quad (5)$$

On the other hand, when the salt concentration is very low, the membrane potential expression becomes

$$E_m = - (RT / F) \ln C_{||} C_l \quad (6)$$

If the membrane potential follows the eqn. (6), the membrane may be referred as a perfectly permselective, where  $t_{app}$  becomes zero and  $P_s$  tends to unity. On the other hand, when membrane potential follows eqn. (5),  $t_{app}$  becomes  $(1-\alpha)$  and  $P_s$  equal to zero. Hence, It can be said that  $P_s$  takes a value between zero and unity depending on the external salt concentration for a given system of a membrane and on an electrolyte pair.

In accordance with eqn. (1), the straight line plot of  $P_s$  values given in Tables 3 & 4 of membranes against  $(4\xi^2 + 1)^{-1/2}$  are shown in Figs. 4 and 5, which confirms the applicability of the irreversible thermodynamic approach to our model system when the average concentration,  $C$  and the

Table 3

The values of permselectivity  $P_s$  of the membrane using various 1:1 electrolytes at different concentration for nickel phosphate membrane.

Electrolyte Concentration/Mol l <sup>-1</sup> $C_{II}/C_I$	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.70	0.79	0.84
$5 \times 10^{-2}/5 \times 10^{-3}$	0.66	0.78	0.77
$1 \times 10^{-2}/1 \times 10^{-3}$	0.52	0.54	0.69
$5 \times 10^{-3}/5 \times 10^{-4}$	0.24	0.39	0.35
$1 \times 10^{-3}/1 \times 10^{-4}$	-0.12	0.05	0.19
$5 \times 10^{-4}/5 \times 10^{-5}$	-0.18	0.02	0.12
$1 \times 10^{-4}/1 \times 10^{-5}$	0.22	-0.13	0.00



**Table 4**

The values of permselectivity  $P_s$  of the membrane using various 1:1 electrolytes at different concentration for cobalt phosphate membrane.

Electrolyte Concentration/Mol l <sup>-1</sup> $C_{II}/C_I$	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.56	0.75	0.77
$5 \times 10^{-2}/5 \times 10^{-3}$	0.50	0.71	0.70
$1 \times 10^{-2}/1 \times 10^{-3}$	0.48	0.63	0.49
$5 \times 10^{-3}/5 \times 10^{-4}$	0.20	0.42	0.43
$1 \times 10^{-3}/1 \times 10^{-4}$	-0.20	0.30	0.19
$5 \times 10^{-4}/5 \times 10^{-5}$	-0.16	-0.02	0.00
$1 \times 10^{-4}/1 \times 10^{-5}$	-0.18	-0.07	-0.10

**Table 5**

The values of effective fixed charge density of nickel phosphate membrane using various 1:1 electrolytes derived from different theories.

Electrolyte	KCl	NaCl	LiCl
Kobataka & Coworkers	$1.9 \times 10^{-3}$	$4.7 \times 10^{-3}$	$4.2 \times 10^{-3}$
Nagasawa et al.	$1.1 \times 10^{-3}$	$2.0 \times 10^{-3}$	$2.2 \times 10^{-3}$
Aizawa et. al.	$1.2 \times 10^{-3}$	$1.75 \times 10^{-3}$	$2.05 \times 10^{-3}$

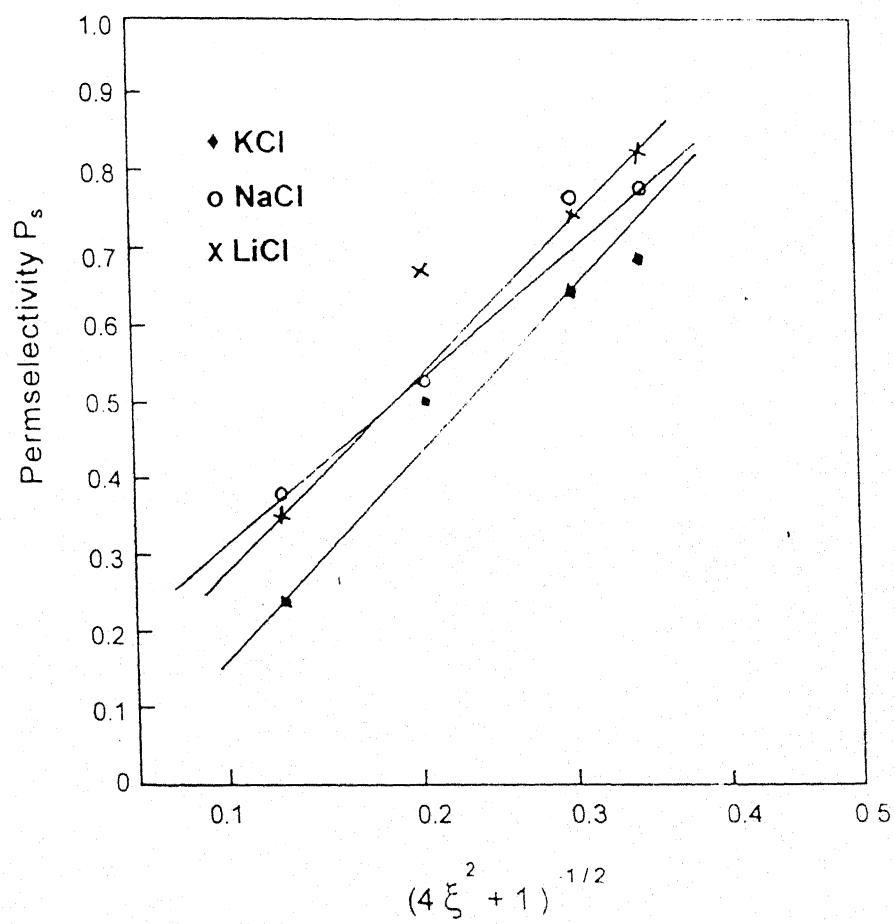


Fig. 4

Plots of permselectivity  $P_s$  vs  $\log(4\xi^2 + 1)^{1/2}$  for nickel phosphate membrane.

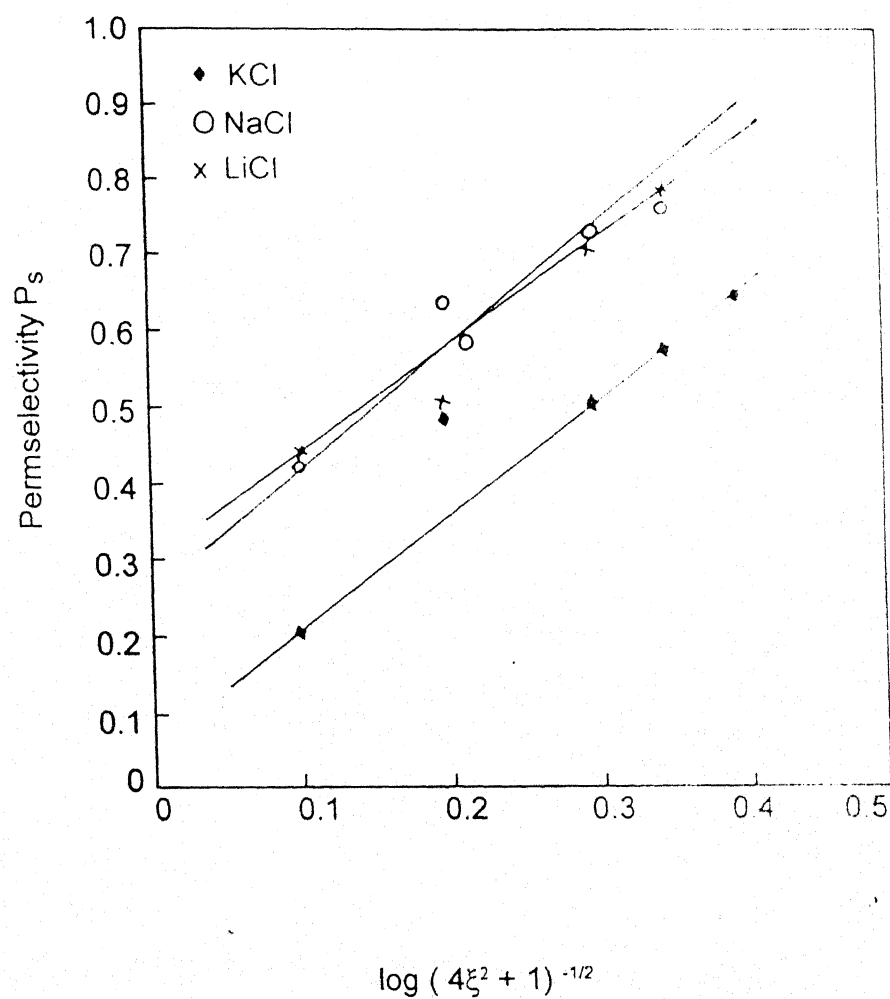


Fig. 5

Plots of permselectivity  $P_s$  vs.  $\log \log ( 4\xi^2 + 1 )^{-1/2}$   
for cobalt phosphate membrane

thermodynamically effective fixed charge density,  $\phi X$ , are of the same magnitude,  $\xi$  become equal to unity and  $P_s$  equal to  $1/\sqrt{5}$ . The magnitude of concentration corresponding to this value of  $P_s$  is a measure of  $\phi X$ .

Another theory developed by Tasaka and coworkers [33] has also been used in the evaluation of magnitude of  $\phi X$ . In the absence of an externally applied electric field or a pressure gradient at the limit of low electrolyte concentration (where the effect of flow of water is negligible), the expression for membrane potential can be written:

$$-E_m = \frac{RT}{F} \ln \frac{C_{||}}{C_{\perp}} \quad (7)$$

whereas at the limit of high electrolyte concentration we have:

$$-E_m = \frac{RT}{F} \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\phi X}{2} \right) 1/C_{\perp} \quad (8)$$

which predicts a linear relationship between  $E_m$  and  $1/C_{\perp}$  and allows the evaluation of  $\phi X$  from the slope of straight lines obtained by plotting  $E_m$  against  $1/C_{\perp}$ .

The effective fixed charge density,  $\phi x$ , has also been related to  $E_m$  and  $t_-$  as [34].

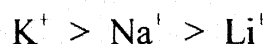
$$\begin{aligned} (F / RT) E_m = & - \ln \gamma + \ln \frac{-\phi X + \sqrt{(\phi X)^2 + 4 C_{||}^2}}{-\phi x + \sqrt{(\phi X + 4 C_{\perp}^2)}} \\ & + (2t_- - 1) \ln \left[ \frac{(1 - 2t_-) \phi X + \sqrt{(\phi X)^2 + 4 C_{||}^2}}{(1 - 2t_-) \phi X + \sqrt{(\phi X)^2 + 4 C_{\perp}^2}} \right] \end{aligned} \quad (9)$$

which can be approximated to eqn. (10) if the membrane is slightly charged.

$$(F/RT) E_m = (2t_- - 1) \ln \gamma + 2 \frac{(y-1)}{\gamma} t_- \frac{(1-t_-)}{C_l} \phi X \quad (10)$$

This equation predicts a straight line plot of  $(F/RT) E_m$  versus  $1/C_l$  at fixed  $\gamma$ , and allows the evaluation of  $t_-$  and  $\phi X$  from the intercept and slope of the linear plot.

Equations (1), (8) and (10) have been utilized to calculate the effective fixed charge density values and the values of transference number ( $t_-$ ) which are given in Tables 5 to 8. The values of transference number  $t_-$  are plotted against  $\log 1/C_l$  as shown in Figs. 6 and 7. The plots of  $P_s$  versus  $\log (C_l + C_{II})/2$  are shown in Figs. 8 and 9,  $E_m$  versus  $1/C_l$  are shown in Figs. 10 and 11, and  $(F/RT) E_m$  versus  $1/C_l$  are shown in Figs. 12 and 13. As the values of  $\phi X$  are quite low, the membranes used in this investigation were expected to have a low negative electrostatic field strength of the fixed charge sites. For such a situation following the Eisenman and Horn [26]; selectivity sequence of metal ions was proposed as :



The same sequence has also already been studied by Eisenman and Horn [26] which also strength to our work.

The selectivity sequence of nickel and cobalt phosphate membranes for the metal ions of the same sign, is also confirmed by various experimental methods as :

**Table 6**

The values of effective fixed charge density of cobalt phosphate membrane using various 1:1 electrolytes derived from different theories.

Electrolyte	KCl	NaCl	LiCl
Kobataka & Coworkers	$5.3 \times 10^{-3}$	$2.5 \times 10^{-3}$	$3.7 \times 10^{-3}$
Nagasawa et al.	$1.1 \times 10^{-3}$	$1.7 \times 10^{-3}$	$2.0 \times 10^{-3}$
Aizawa et. al.	$1.7 \times 10^{-3}$	$1.3 \times 10^{-3}$	$1.8 \times 10^{-3}$

**Table 7**

Transference number  $t_+$  of coions from derived from observed membrane potential at various electrolyte concentration through nickel phosphate membrane.

Electrolyte Concentration/Mol $l^{-1}$ $C_{II}/C_I$	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.85	0.85	0.84
$5 \times 10^{-2}/5 \times 10^{-3}$	0.83	0.84	0.82
$1 \times 10^{-2}/1 \times 10^{-3}$	0.76	0.70	0.76
$5 \times 10^{-3}/5 \times 10^{-4}$	0.62	0.60	0.55
$1 \times 10^{-3}/1 \times 10^{-4}$	0.46	0.42	0.46
$5 \times 10^{-4}/5 \times 10^{-5}$	0.41	0.41	0.43
$1 \times 10^{-4}/1 \times 10^{-5}$	0.34	0.34	0.37

Table 8

Transference number  $t_-$  of coions from derived from observed membrane potential at various electrolyte concentration through cobalt phosphate membrane.

Electrolyte Concentration/Mol l <sup>-1</sup> $C_{II}/C_I$	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.78	0.82	0.81
$5 \times 10^{-2}/5 \times 10^{-3}$	0.75	0.80	0.77
$1 \times 10^{-2}/1 \times 10^{-3}$	0.74	0.68	0.63
$5 \times 10^{-3}/5 \times 10^{-4}$	0.60	0.62	0.58
$1 \times 10^{-3}/1 \times 10^{-4}$	0.69	0.54	0.45
$5 \times 10^{-4}/5 \times 10^{-5}$	0.42	0.41	0.37
$1 \times 10^{-4}/1 \times 10^{-5}$	0.47	0.37	0.33

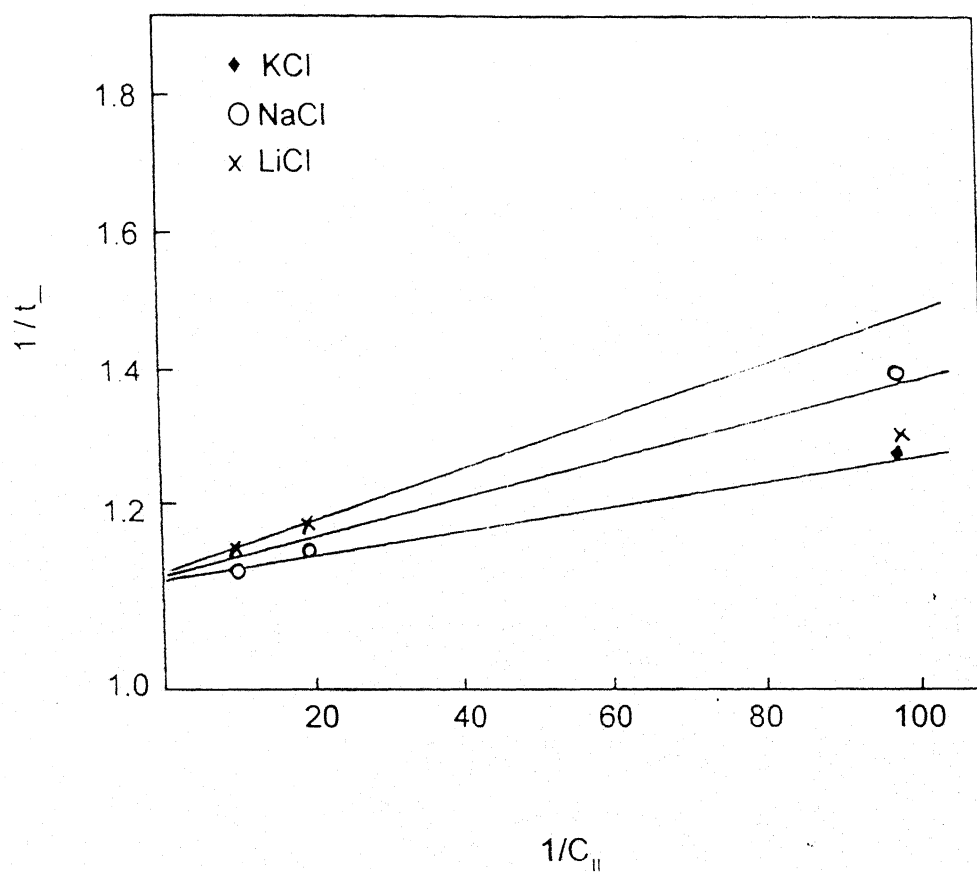


Fig 6

Plots of transference number ( $t_-$ ) against  $1/C_{II}$  of various 1:1 electrolytes at different concentration across nickel phosphate membrane.



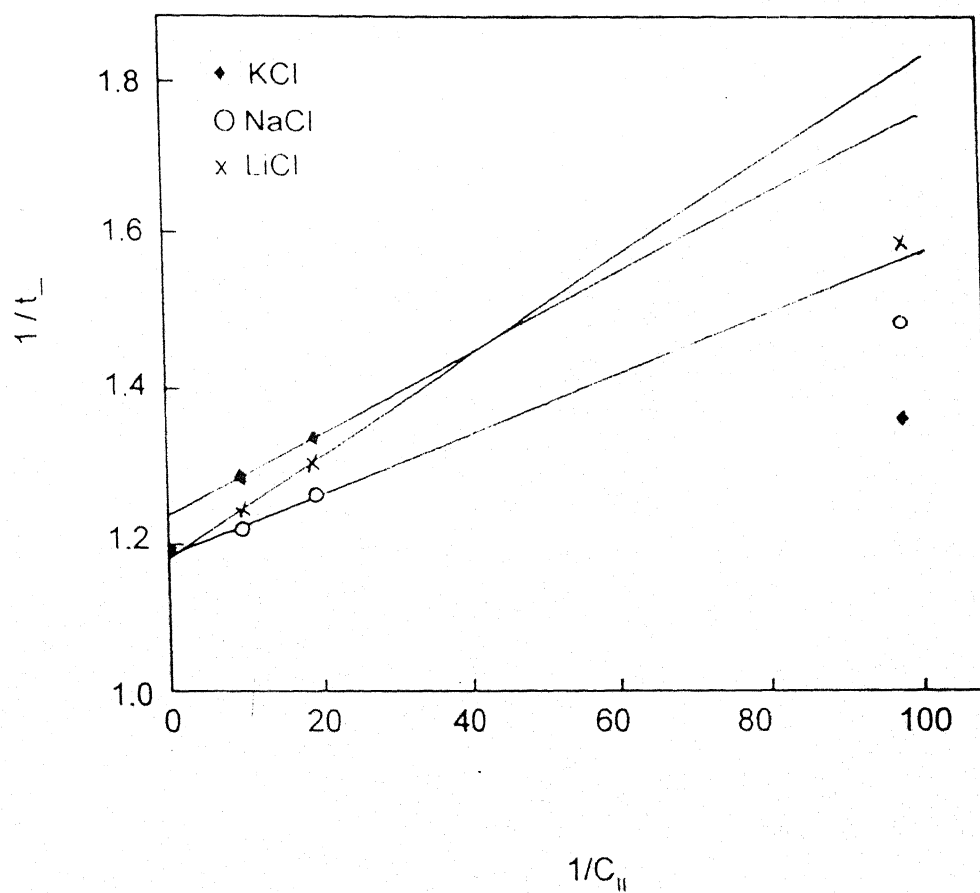


Fig 7

Plots of transference number ( $t_-$ ) against  $1/C_{II}$  of various 1:1 electrolytes at different concentration across cobalt phosphate membrane

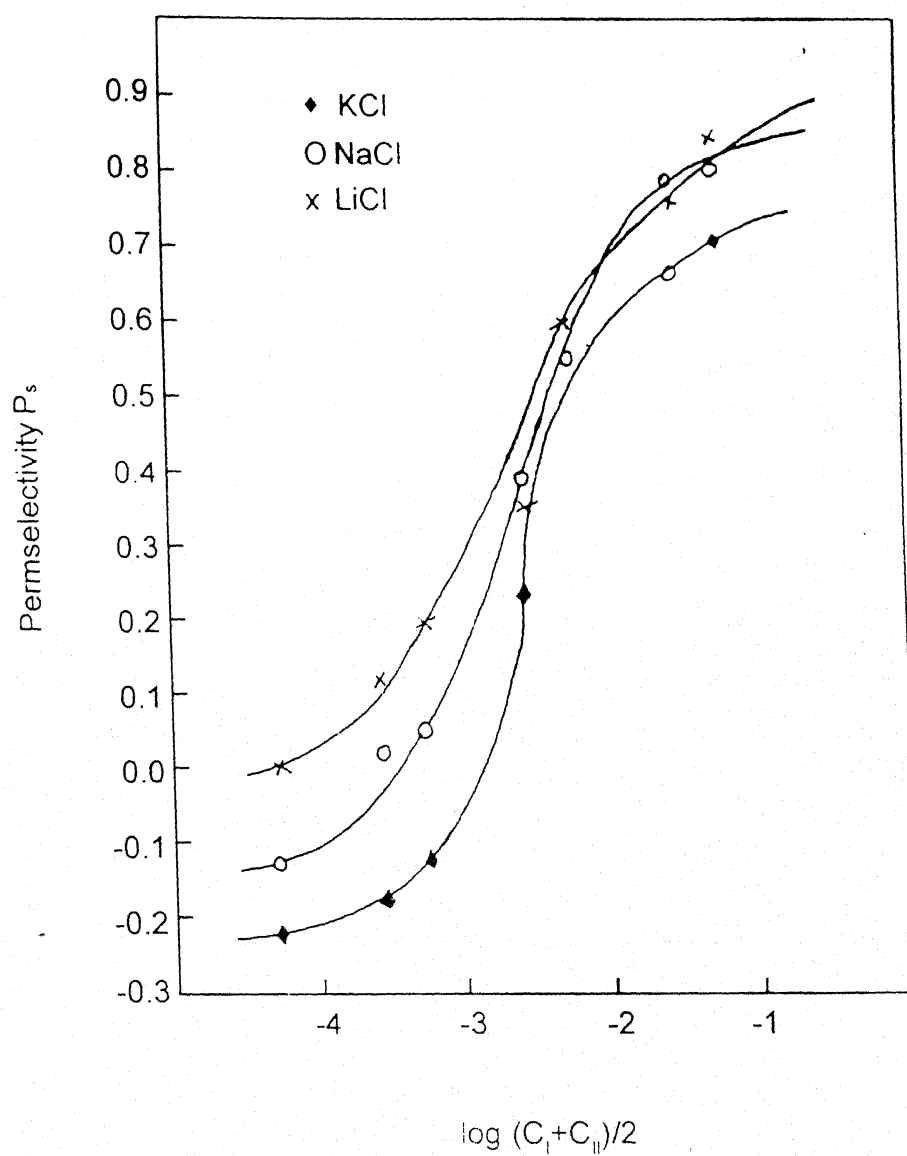


Fig 8

Plots of permselectivity  $P_s$  vs.  $\log (C_I + C_{II})/2$  for nickel phosphate membrane.

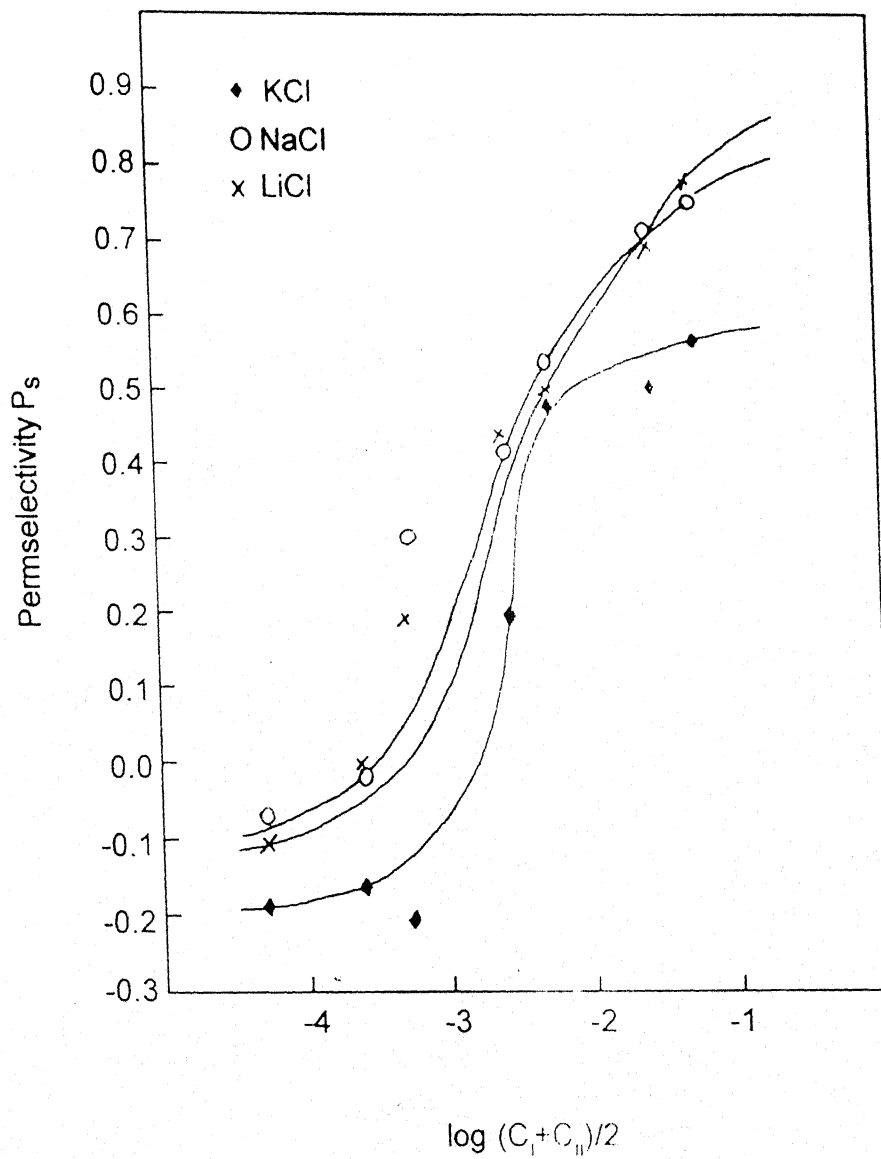


Fig 9

Plots of permeability  $P_s$  vs.  $\log (C_I + C_{II})/2$  for cobalt phosphate membrane.

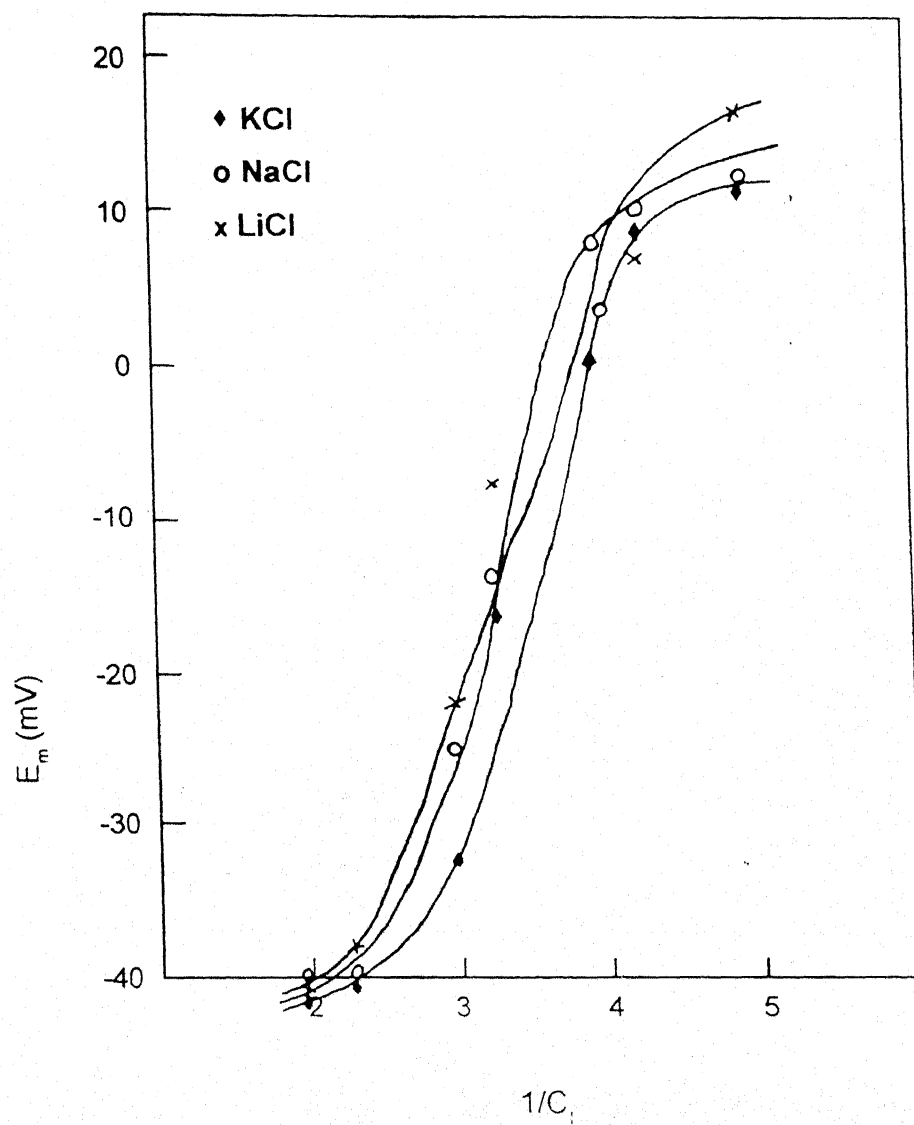


Fig 10

Plots of Membrane Potential  $E_m$  (mV) vs.  $1/C_1$  for nickel phosphate membrane.

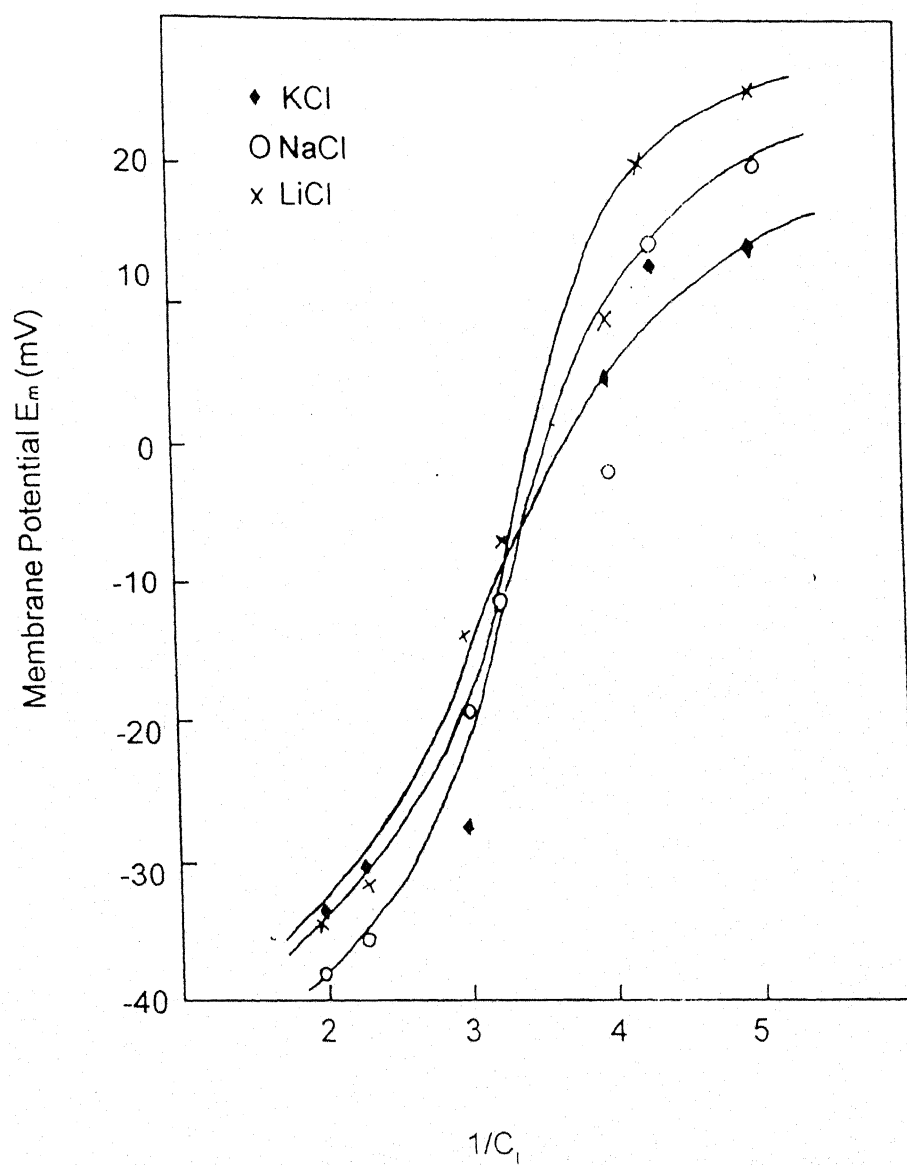


Fig 11

Plots of membrane potential  $E_m$  (mV) vs.  $1/C_i$  for cobalt phosphate membrane.

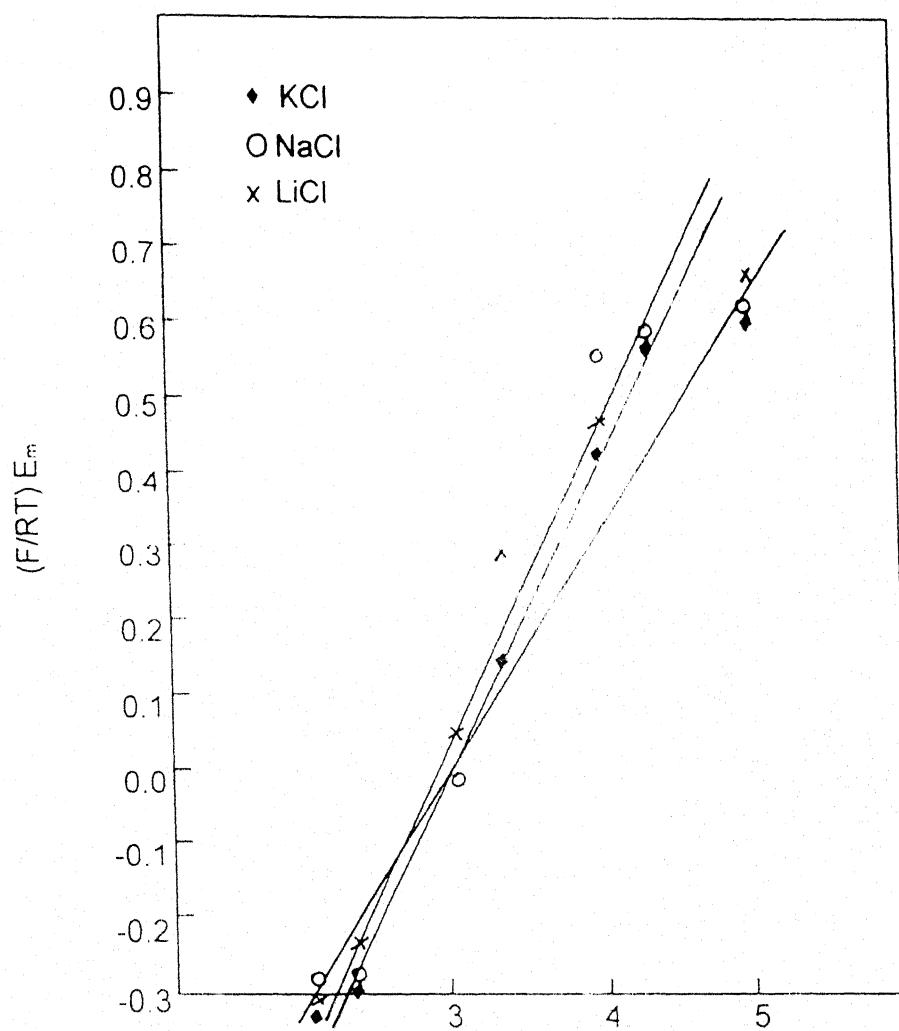


Fig. 12

Plots of  $(F/RT) E_m$  (mV) vs.  $1/C_1$  for  
nickel phosphate membrane.

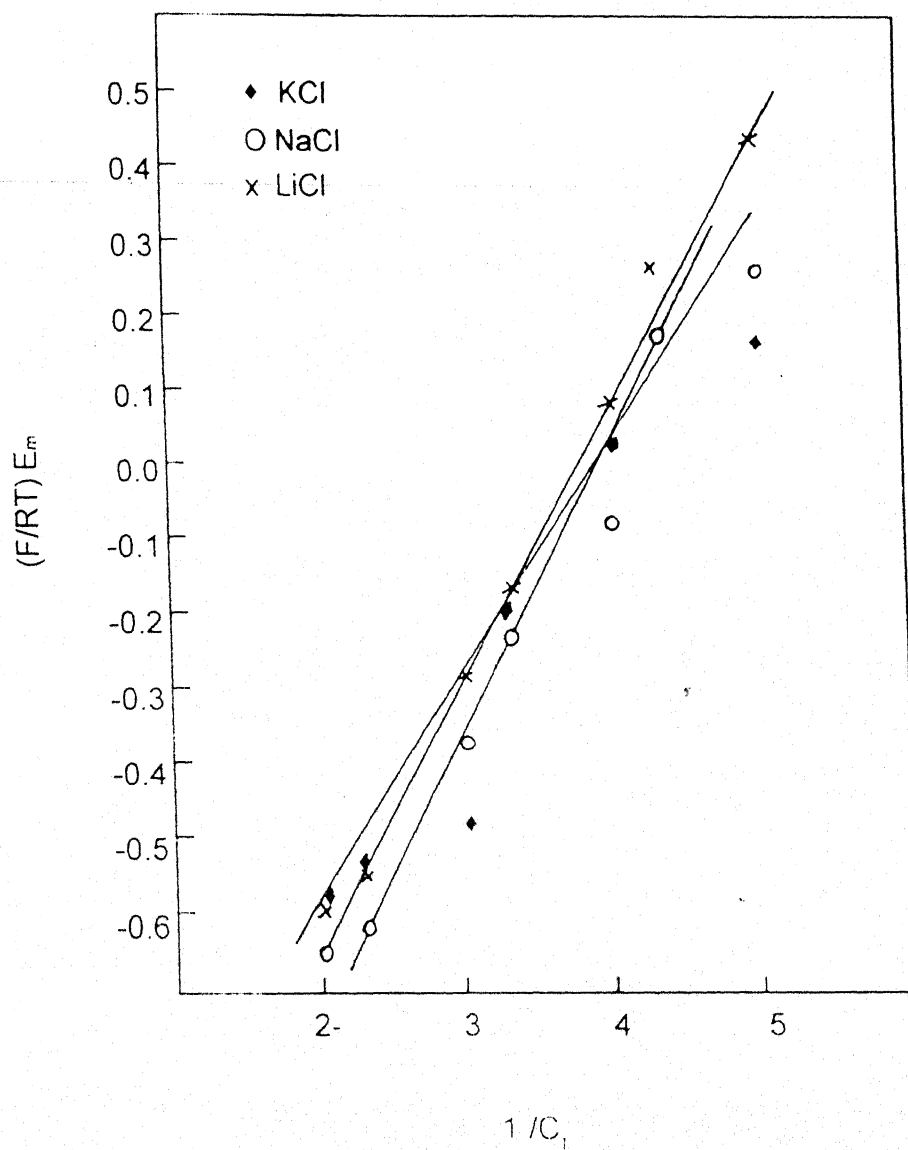


Fig 13

Plots of  $(F/RT) E_m$  (mV) vs.  $1/C_i$  for cobalt phosphate membrane.

### BI-IONIC METHOD :

The steady e.m.f. of a biionic cell, containing two electrolytes of the type  $iX$  and  $jX$  (or  $iX$  and  $iY$ ) separated by a membrane, is called the biionic potential (BIP) [35], which is measure of the selectivity of the membrane for ions of the same sign. The BIP has also been considered by Hellferich [15], in accordance with the concepts of the TMS theory [9,10], as being the algebraic sum of the two interfacial potentials and an internal diffusion potential. A complete mathematical discussion under the conditions: (a) membrane diffusion control, (b) film diffusion control, and (c) coupled membrane film diffusion control has been presented [15]. For a general case involving complete membrane diffusion control, the total BIP for counter ions is given by

$$E = \frac{RT}{zF} \ln \frac{\overline{D}_i a_j K_i}{\overline{D}_j a''_j \overline{V}_i K_j} = \ln \left[ K_{ji} \left( \frac{\overline{D}_i a'_i \overline{v}_j}{\overline{D}_j a''_j \overline{v}_i} \right) \right] \quad (11)$$

where  $a'_j/a''_j$ ,  $\overline{D}_i/\overline{D}_j$ ,  $\overline{V}_i/\overline{V}_j$  are the ratio of the activities, diffusion coefficients and the activity coefficients of the counter ions  $i$  and  $j$ , respectively. Overbars refer the phenomena in the membrane phase;  $R$ ,  $T$ ,  $z$  and  $F$  have their usual meanings. Using the Einstein relation  $\overline{D}_i = U_i RT$  and the generalized Nernst equation in which the permeability ratios are independent of the external electrolyte solution [14,36] the eqn. (11) reduces to the form

$$E = \frac{RT}{zF} \ln \left[ \frac{a'_i \overline{U}_i}{a''_j \overline{U}_j} K_{ji} \right] = \frac{RT}{zF} \ln \left[ \frac{a'_i \overline{P}_i}{a''_j \overline{P}_j} \right] \quad (12)$$



equation (12) gives

$$\overline{P}_i / \overline{P}_j = K_{ij} \overline{U}_i / \overline{U}_j$$

This equation has also been derived by Sandblom and Eisenman [17] from thermodynamic treatment for fixed site membranes which implies that the permeability ratio is quite generally related to the ion exchange equilibrium constant  $K_{ij}$  and the ratio of mobilities of the critical ions. Further, using the well known relation

$$\overline{U}_i / \overline{U}_j = \overline{\lambda}_i / \overline{\lambda}_j \quad (14)$$

where  $\overline{\lambda}_i$  is the conductivity of the membrane when it is wholly in i form and  $\overline{\lambda}_j$  is the conductivity of the membrane when it is wholly in the j form.

The quantity  $\overline{P}_i / \overline{P}_j$  is considered truly a membrane property (17). It is Independent of the changes made in the activities  $a_i$  and  $a_j$  of the external solution. Thus it is apparent from eqn. (12) that a plot of  $\log a_i$  against potential for a constant  $a_j$  should give a straight line. Similarly a straight line should be obtained if  $a_j$  is varied and  $a_i$  is kept constant. Both these lines. should show potential changes of  $RT/F$  or 59.2 mV at 25° C for each tenfold changes in activity when membranes are separating 1:1 electrolytes. Accordingly, BIP values across parchment supported nickel and cobalt phosphate membranes were determined for various electrolyte

pairs, viz. KCl-NaCl, KCl - LiCl and NaCl-LiCl, taking the concentration of one of the electrolyte constant (0.01 M) and varying the concentration of the other electrolyte between 0.001 M to 0.01 M. In second set of experiment the concentration of other electrolyte was kept constant and the concentration of the first electrolyte was varied in same range. The biionic potentials thus observed were plotted against logarithm of the mean molal activity. Two sets of straight lines in accordance with the expectation of eqn. (12) are obtained as shown in Figs. 14 and 15. The straight lines confirm the views of Beg and Eisenman [14,36] that the permeability ratios are independent of external solution conditions. In order to derive the values of the permeability ratio, these straight lines were extended to cut the activity axis at zero potential. Thus two sets of  $a_i$  and  $a_j$  values for which potential  $E$  was zero, were obtained. At zero potential the ratio  $a_i / a_j$  was equal to  $\bar{P}_i / \bar{P}_j$ . The values of  $\bar{P}_i / \bar{P}_j$  derived. In this way for the nickel and cobalt phosphate membranes for different electrolyte pairs are as follows :

$$\bar{P}_{K^+} / \bar{P}_{Na^+} = 1.72, \quad \bar{P}_{K^+} / \bar{P}_{Li^+} = 1.50, \quad \bar{P}_{Na^+} / \bar{P}_{Li^+} = 1.36$$

for nickel phosphate membrane

$$\bar{P}_{K^+} / \bar{P}_{Na^+} = + 1.99, \quad \bar{P}_{K^+} / \bar{P}_{Li^+} = 1.71, \quad \bar{P}_{Na^+} / \bar{P}_{Li^+} = 1.18$$

for cobalt phosphate membrane.

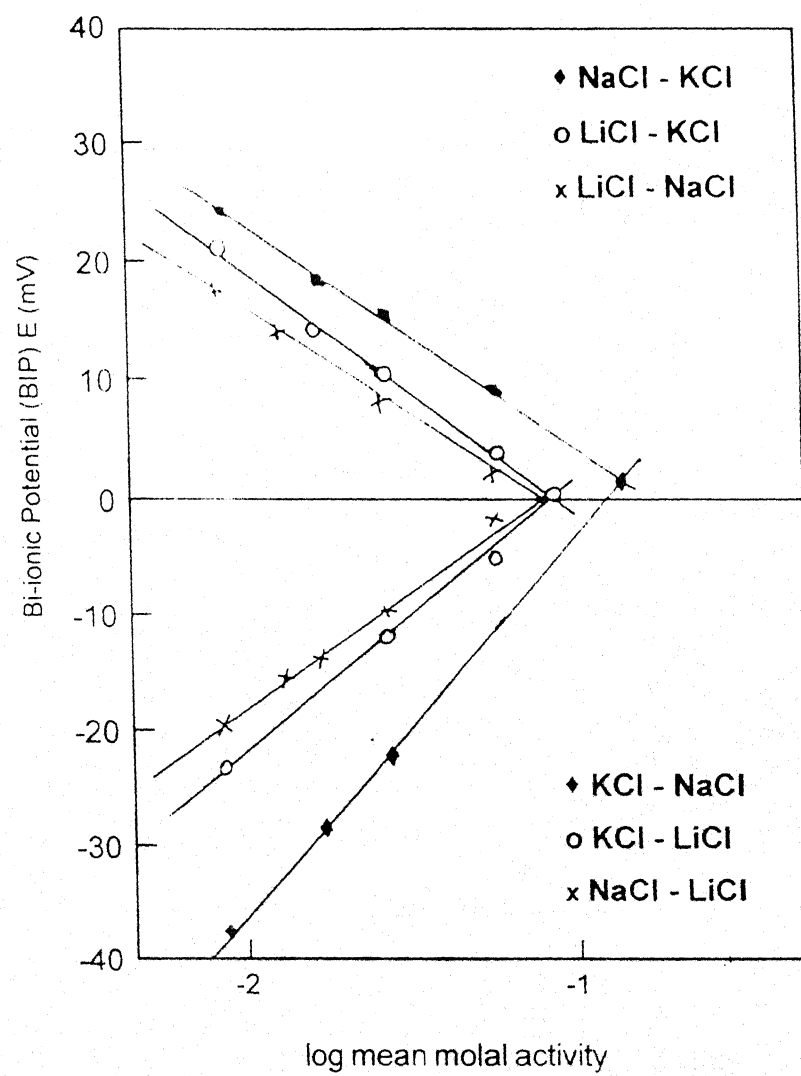


Fig 14

Plots of Biionic potential (BIP)  $E$  (mV) vs. logarithm of mean molal activity for nickel phosphate membrane.

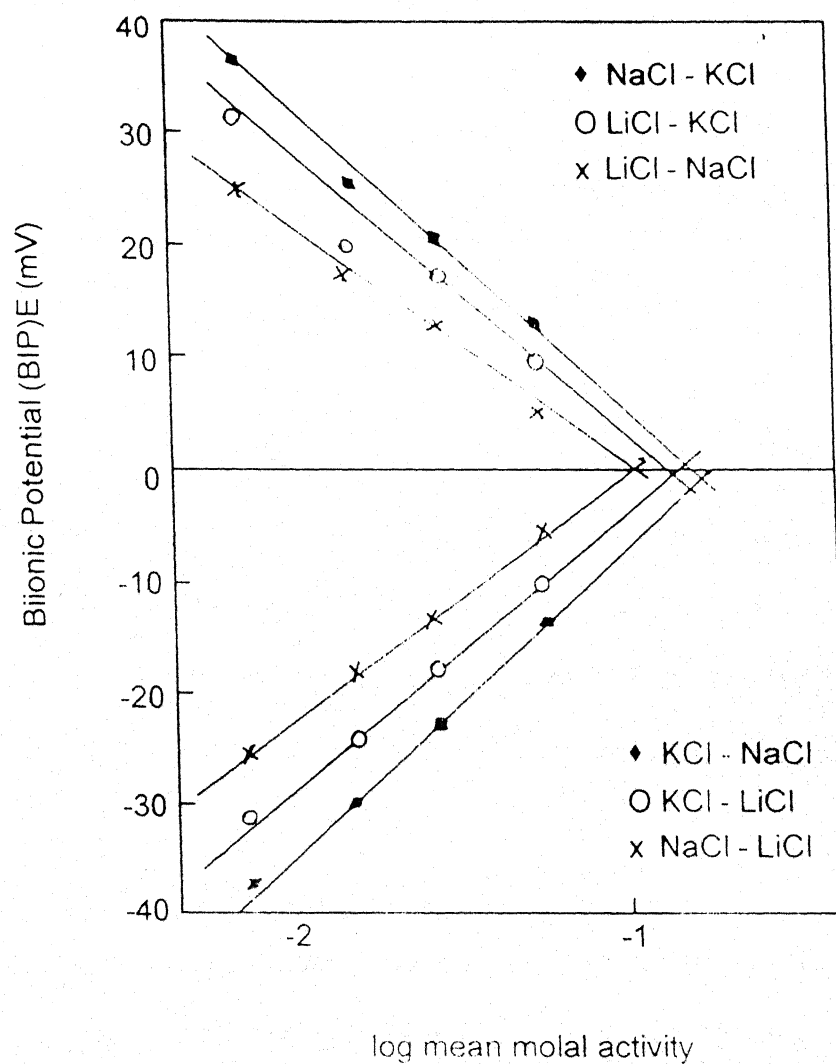
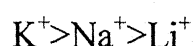


Fig. 15

Plots of biionic potential (BIP) E (mV) vs logarithm of mean molal activity for cobalt phosphate membrane

The values of  $\bar{P}_i/\bar{P}_j$  are generally low which point towards the fact that the membranes are relatively more imbibed in an equilibrium water content [37]. The values of the intramembrane permeability ratio also refer to the selectivity sequence of the membranes for the cations of the following order:



This order of selectivity on the basis of the Eisenman-Sherry model of membrane selectivity [36,38,39] points towards the weak field strength of the charge groups attached to the membrane matrix. This is in accordance with our earlier findings of charge density (charge density  $\approx 10^{-3} \text{ mol l}^{-1}$ ) determinations of nickel and cobalt phosphate membranes [4].

Biionic potential measurements were also carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The BIP values were low when the membrane was used to separate concentrated electrolyte solutions whereas, it increased with decreasing salt concentrations. In this way experimentally observed values of BIP across both membranes are given in Tables 9 and 10 and this change is depicted in Figs. 16 and 17. The permeability ratio  $\bar{P}_i/\bar{P}_j$

**Table 9**

Experimental values of biionic potential (BIP) E (mV) across nickel phosphate membrane at  $25 \pm 0.1^\circ\text{C}$

<b>Electrolyte</b>	<b>KCl-NaCl</b>	<b>KCl-LiCl</b>	<b>NaCl - LiCl</b>
Concentration / Mol l <sup>-1</sup>			
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.26	-3.94	-2.26
$5 \times 10^{-2} / 5 \times 10^{-2}$	4.54	-2.74	-2.03
$1 \times 10^{-2} / 1 \times 10^{-2}$	8.57	2.60	2.24
$5 \times 10^{-3} / 5 \times 10^{-3}$	11.65	3.45	4.15
$1 \times 10^{-3} / 1 \times 10^{-3}$	19.84	16.00	13.46

**Table 10**

Experimental values of biionic potential (BIP) E (mV) across cobalt phosphate membrane at  $25 \pm 0.1^\circ\text{C}$

<b>Electrolyte</b>	<b>KCl-NaCl</b>	<b>KCl-LiCl</b>	<b>NaCl - LiCl</b>
Concentration / Mol l <sup>-1</sup>			
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.41	-4.52	-4.21
$5 \times 10^{-2} / 5 \times 10^{-2}$	2.55	-2.46	-2.46
$1 \times 10^{-2} / 1 \times 10^{-2}$	6.80	2.62	0.99
$5 \times 10^{-3} / 5 \times 10^{-3}$	13.30	5.11	3.45
$1 \times 10^{-3} / 1 \times 10^{-3}$	14.80	18.50	9.76

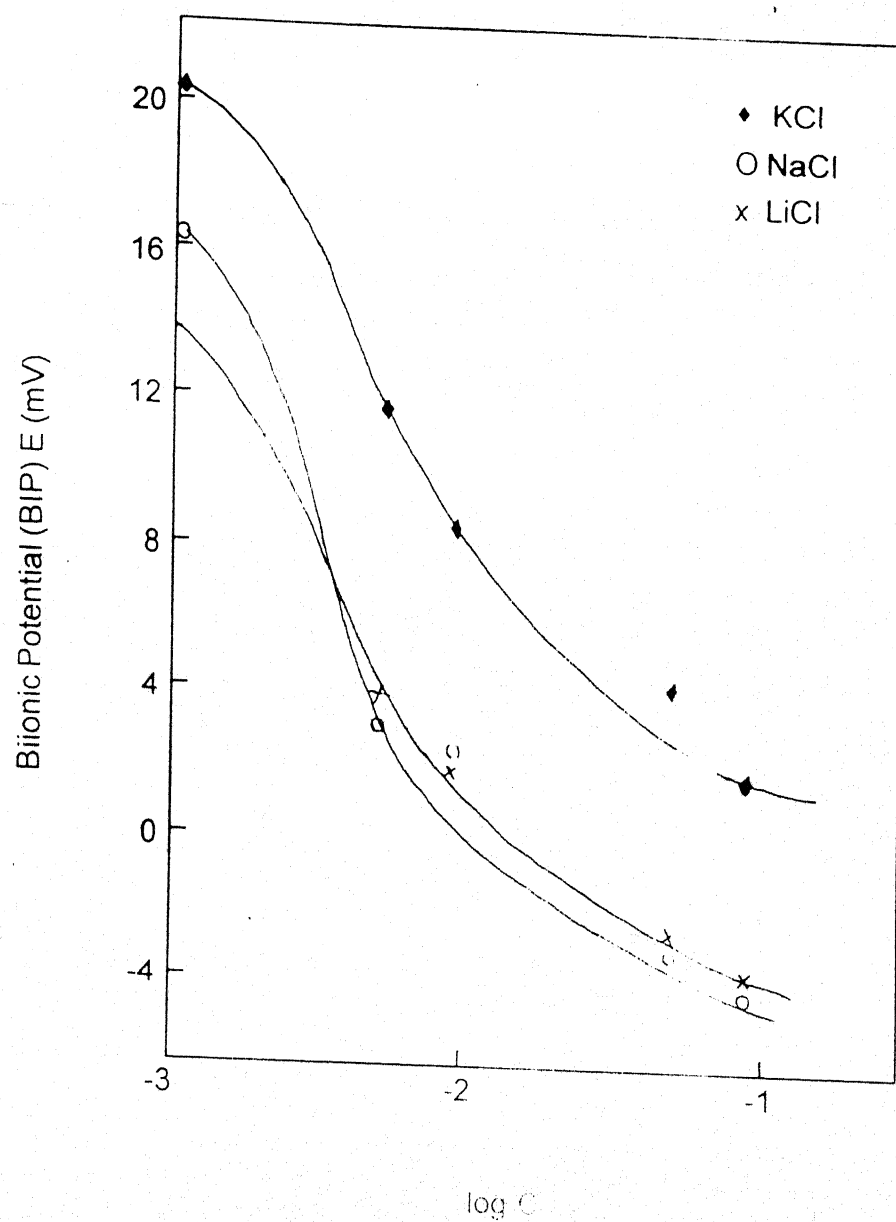


Fig. 16

Plots of biionic potential (BIP)  $E$  (mV) vs.  $\log C$  for nickel phosphate membrane.

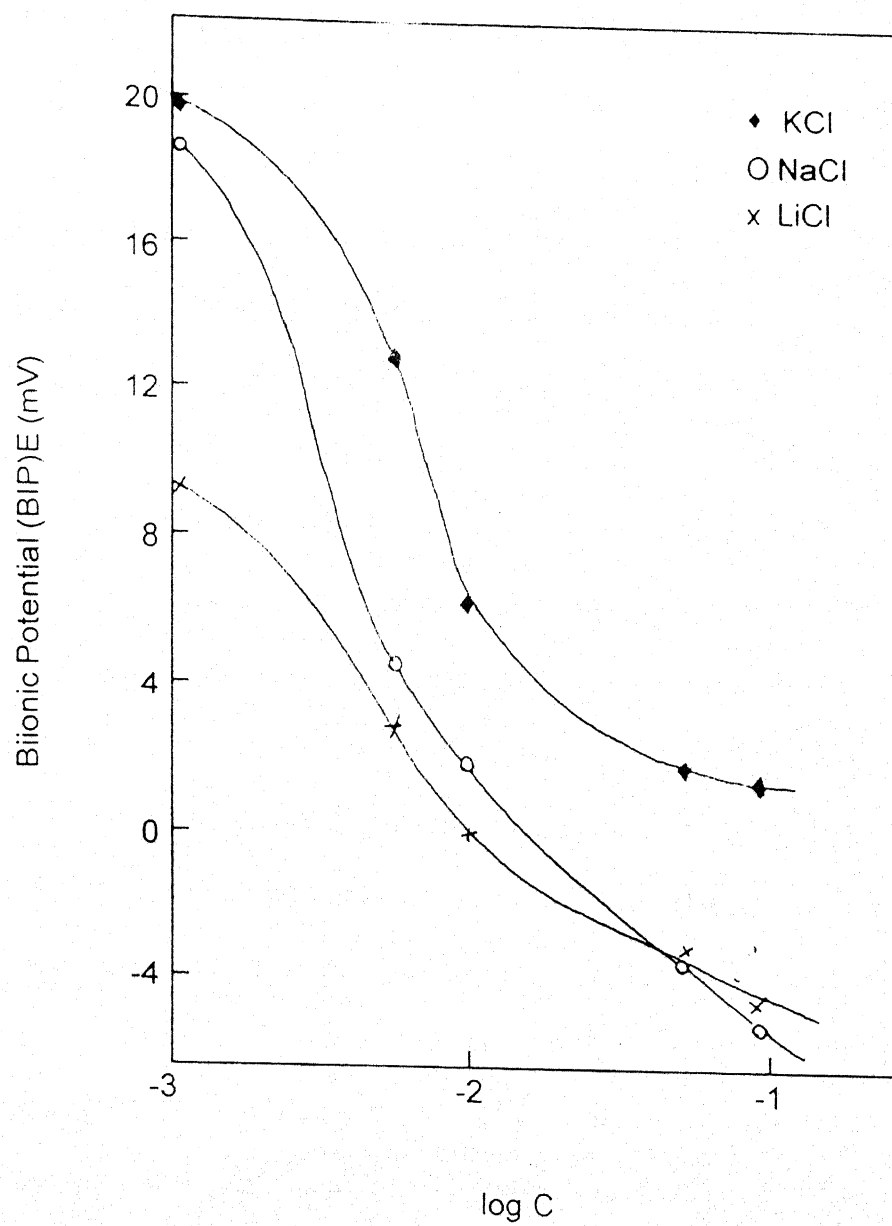


Fig. 17

Plots of biionic potential (BIP)  $E$  (mV) vs.  $\log C$  for cobalt phosphate membrane.



calculated from BIP values using eqn. (12) given in Tables 11 and 12, were also seen concentration dependent. The variation in BIP caused by the changes produced in the permeability ratio may be ascribed due to structural changes produced at the membrane solution interfaces. Parchment supported inorganic precipitated membranes contain exchangeable groups as part of its structure which may account for its negative charge. The exchangeable cations will be free to move in the pores. Within the pores there will be a diffuse ionic atmosphere from the charged wall. Since the membrane under investigation carries low ionic charge densities ( i. e., charge density of the order  $1 \times 10^{-3} \text{ mol l}^{-1}$ ), anion encroachment into membrane seems to be the most probable phenomenon. The thickness of the atmosphere depends upon the electrolyte concentration. In very dilute solutions of electrolyte, the thickness of anions becomes so great that only cations are present in the pores and the membranes becomes impermeable to anions, which is actually a condition necessary for the derivation of eqn. (12) with constant permeability ratio. Thus the best data on  $P_i / P_j$  are that from the most dilute solutions. It may therefore, be concluded that the existence of an expression for  $E$  with constant permeability ratios can not be characteristic of all the membranes but it is restricted to certain physical situations, most notably those in which a membrane is permeable only to species of one sign. This is an agreement with the mathematical treatment advanced by Sandblom and Eisenman [17].

Table 11

Values of the intramembrane permeability ratios ( $\bar{P}_i/\bar{P}_j$ ) of various 1:1 electrolyte ion pairs for nickel phosphate membrane.

Electrolyte ion pair	KCl-NaCl	KCl-LiCl	NaCl - LiCl
Concentration / Mol l <sup>-1</sup>			
1x10 <sup>-1</sup> /1x10 <sup>-1</sup>	1.09	0.80	0.88
5x10 <sup>-2</sup> /5x10 <sup>-2</sup>	1.19	0.90	0.92
1x10 <sup>-2</sup> /1x10 <sup>-2</sup>	1.44	1.09	1.09
5x10 <sup>-3</sup> /5x10 <sup>-3</sup>	1.57	1.14	1.19
1x10 <sup>-3</sup> /1x10 <sup>-3</sup>	2.17	1.86	1.68

Table 12

Values of the intramembrane permeability ratios ( $\bar{P}_i/\bar{P}_j$ ) of various 1:1 electrolyte ion pairs for cobalt phosphate membrane.

Electrolyte ion pair	KCl-NaCl $\bar{P}_{K^+} / \bar{P}_{Na^+}$	KCl-LiCl $\bar{P}_{K^+} / \bar{P}_{Li^+}$	NaCl - LiCl $\bar{P}_{Na^+} / \bar{P}_{Li^+}$
Concentration / Mol l <sup>-1</sup>			
1x10 <sup>-1</sup> /1x10 <sup>-1</sup>	1.10	0.83	0.84
5x10 <sup>-2</sup> /5x10 <sup>-2</sup>	1.24	0.90	0.90
1x10 <sup>-2</sup> /1x10 <sup>-2</sup>	1.30	1.10	1.04
5x10 <sup>-3</sup> /5x10 <sup>-3</sup>	1.68	1.22	1.14
1x10 <sup>-3</sup> /1x10 <sup>-3</sup>	2.16	1.45	1.46

Table 13

Observed values of membrane conductance (Sm<sup>-1</sup>) for monovalent electrolyte at 25±0.1°C across nickel phosphate membrane.

Electrolyte	KCl-NaCl	KCl-LiCl	NaCl - LiCl
Concentration / Mol l <sup>-1</sup>			
1x10 <sup>-1</sup> /1x10 <sup>-1</sup>	0.91	0.52	0.35
5x10 <sup>-2</sup> /5x10 <sup>-2</sup>	1.6	1.0	0.82
1x10 <sup>-2</sup> /1x10 <sup>-2</sup>	3.4	2.6	2.2
5x10 <sup>-3</sup> /5x10 <sup>-3</sup>	4.0	3.2	2.8
1x10 <sup>-3</sup> /1x10 <sup>-3</sup>	8.0	7.0	6.8

In order to have a knowledge of selectivity  $K_{ij}$  from the predetermined values of  $\bar{P}_i/\bar{P}_j$ , the ratio of electrical conductivities  $\bar{\lambda}_i/\bar{\lambda}_j$ , as demanded by eqn. (14) must be known. Membrane conductance measurements were carried out when it was wholly in the form i or wholly in the form j. The values of membrane conductance at various electrolyte concentration of both the membranes are given in Tables 13 and 14, which are relatively more dependent upon the concentration of the electrolyte within the membranes as shown in Figs. 18 and 19. This implies that the membranes have a relatively high Donnan uptake of anion and a low selectivity constant value. This is in agreement with the findings of Heyman and Rabinov [40], Spiegler et al. [41] and our own findings with ion exchange membranes [4-8]. The values of selectivity,  $K_{ij}$  evaluated from the ratio of electrical conductivities  $\bar{\lambda}_i/\bar{\lambda}_j$  and the intramembrane permeability ratio  $\bar{P}_i/\bar{P}_j$  using eqn. (14) are given in Tables 15 and 16.

#### **MIXTURE METHOD :**

To assess the selectivity sequence of the membranes for the cations, values of potentiometric selectivity constant  $K_{ij}^{Pot}$  have been evaluated using the methods developed by Dole [42], and modified and improved by Buck et al. [43, 44]. However, a number of methods [45] have been suggested for the determination of selectivity constant by taking the mixture of electrolytes across the membrane and measuring the electrical potentials developed. The general equation (eqn. 15) for

**Table 14**

Observed values of membrane conductance ( $\text{Sm}^{-1}$ ) for monovalent electrolyte at  $25 \pm 0.1^\circ\text{C}$  across cobalt phosphate membrane.

Electrolyte Concentration / $\text{Mol l}^{-1}$	KCl-NaCl	KCl-LiCl	NaCl - LiCl
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.64	0.62	0.41
$5 \times 10^{-2} / 5 \times 10^{-2}$	1.04	1.02	0.70
$1 \times 10^{-2} / 1 \times 10^{-2}$	3.6	3.5	2.4
$5 \times 10^{-3} / 5 \times 10^{-3}$	4.6	4.6	3.2
$1 \times 10^{-3} / 1 \times 10^{-3}$	8.0	7.8	5.0

**Table 15**

Values of the selectivity  $K_{ji}$  derived from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte concentration for nickel phosphate membrane.

Selectivity Concentration / $\text{Mol l}^{-1}$	$K_{\text{NaK}}$	$K_{\text{LiK}}$	$K_{\text{LiNa}}$
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.62	0.33	0.6
$5 \times 10^{-2} / 5 \times 10^{-2}$	0.74	0.46	0.76
$1 \times 10^{-2} / 1 \times 10^{-2}$	1.10	0.72	0.93
$5 \times 10^{-3} / 5 \times 10^{-3}$	1.25	0.76	0.99
$1 \times 10^{-3} / 1 \times 10^{-3}$	1.80	1.43	1.52

**Table 16**

Values of the selectivity  $K_{ji}$  derived from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte concentration for cobalt phosphate membrane.

<b>Selectivity</b> Concentration / Mol l <sup>-1</sup>	<b>K<sub>NaK</sub></b>	<b>K<sub>LiK</sub></b>	<b>K<sub>LiNA</sub></b>
1x10 <sup>-1</sup> /1x10 <sup>-1</sup>	1.06	0.53	0.56
5x10 <sup>-2</sup> /5x10 <sup>-2</sup>	1.20	0.63	0.67
1x10 <sup>-2</sup> /1x10 <sup>-2</sup>	1.25	0.73	0.72
5x10 <sup>-3</sup> /5x10 <sup>-3</sup>	1.60	0.87	1.03
1x10 <sup>-3</sup> /1x10 <sup>-3</sup>	2.07	1.33	1.04

**Table 17**

Values of potentiometric selectivity constant ( $K_{ij}^{Pot}$ ) for the nickel phosphate membrane at various electrolyte concentration.

<b>Selectivity constant</b> Concentration / Mol l <sup>-1</sup>	<b>K<sub>K-Na</sub></b>	<b>K<sub>K-Li</sub></b>	<b>K<sub>Na - Li</sub></b>
1x10 <sup>-1</sup>	0.64	0.35	0.49
1x10 <sup>-2</sup>	1.10	1.20	1.34
1x10 <sup>-3</sup>	4.01	5.20	2.18

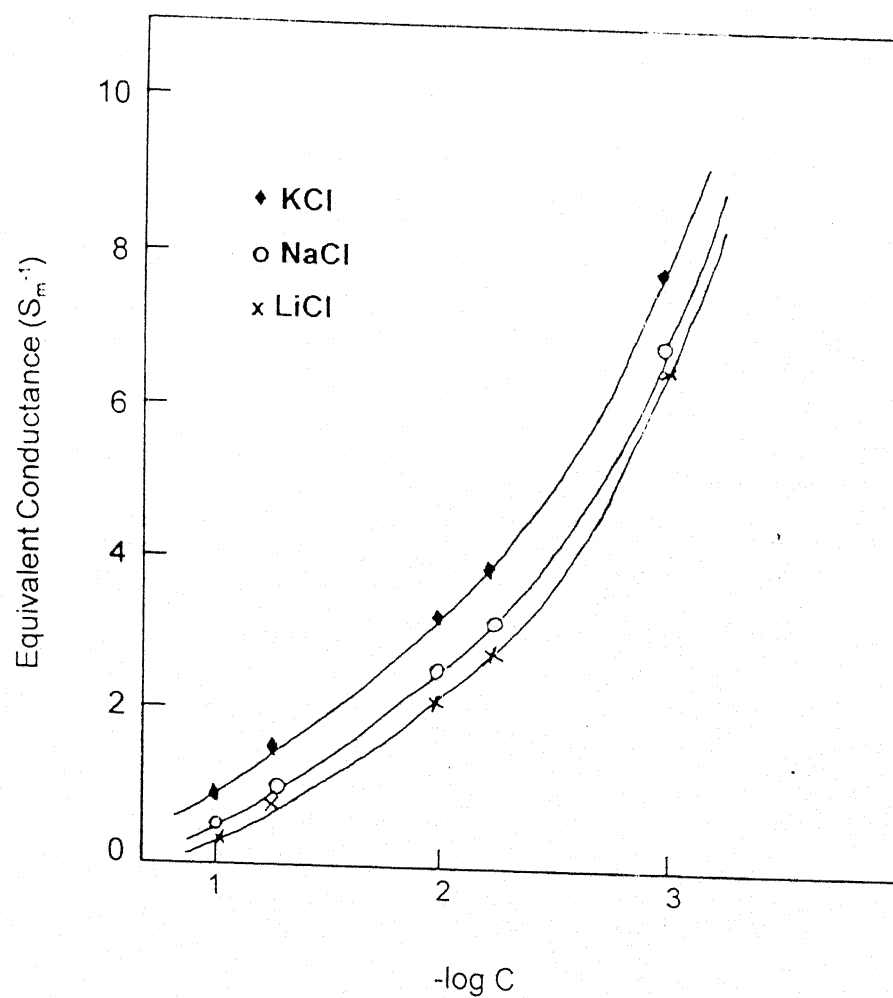


Fig. 18

Typical plots of equivalent conductance ( $S_m^{-1}$ ) vs.  $-\log C$  for nickel phosphate membrane.

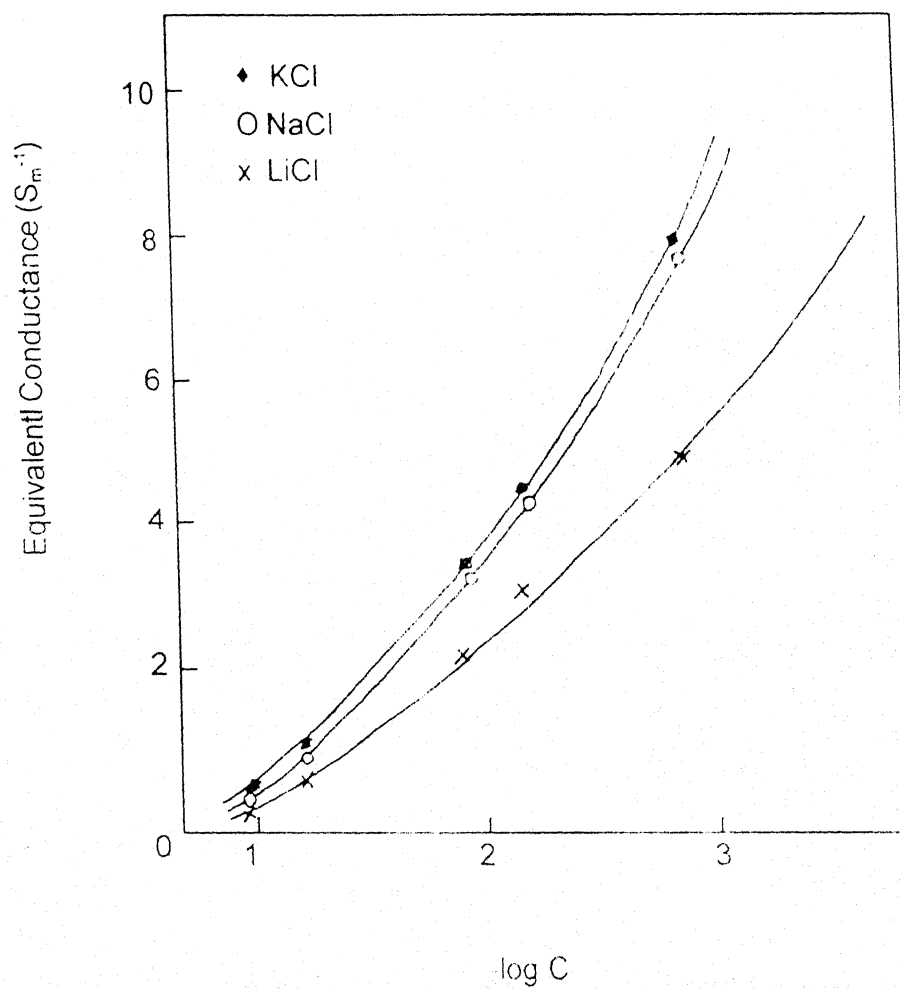


Fig. 19

Typical plots of equivalent conductance ( $S_m^{-1}$ ) vs.  $-\log C$  for cobalt phosphate membrane.



membrane potential E in an electrochemical cell of the type

Electrolyte solution (')	Membrane	Electrolyte solution (")
(i + j)		i or i. or (i + j)

has often been used to derive the value of  $K_{ij}^{pot}$  of membrane electrolyte system.

$$E = \frac{nRT}{F} \ln [(a_i')^{1/n} + (K_{ij}^{pot} a_j')^{1/n}] / [(a_i'')^{1/n} + (K_{ij}'')^{1/n}] \quad (15)$$

where

$$K_{ij}^{pot} = K_{ij} (\bar{U}_j / \bar{U}_i)^{1/n}$$

If  $n=1$  and the concentrations on (") side are held constant then eqn. (15) gives

$$E = const + (RT / F) \ln [a_i' + (K_{ij}^{pot} a_j')] \quad (16)$$

The equation (16) is considered a normal form for ideal behaviour of ion selective electrode responsive to species i and j. If the response for cation is more positive for solutions of species i than for j at equal activities then  $K_{ij}^{pot}$  is than unity and the electrode is more sensitive to i to j [20]. Equation (16) has been used in various ways for the evaluation of potentiometric selectivity constant  $K_{ij}^{pot}$ . Various aspects of eqn. (16) for

the evaluation of  $K_{ij}^{\text{Pot}}$  were reviewed by Lakshminarayanaiah [45]. Mixture methods based on eqn. (16) were first developed and used extensively by Lengyel and Blum [46] and later by Eisenman [47]. Srinivasan and Rechnitz [48] examined several methods for the determination of  $K_{ij}^{\text{Pot}}$  while Pungor and Toth [49,50] strongly recommended another form of the mixture method is the titration procedure of Dole [42] which was modified and improved by Buck et al. [20,43,44]. This method provides extensive sets of data for the determination of  $K_{ij}^{\text{Pot}}$  (apparent). In this method a set of mixture response potentials  $\Delta E_{ij}$  were measured and the selectivity coefficient were calculated using the equation eqn. (17).

$$\ln K_{ij}^{\text{Pot}} (\text{apparent}) = \ln \left\{ \exp[\Delta E_{ij} - E_i] / S \right\} - 1 \} - \ln (a_i / a_j) \quad (17)$$

where  $S$  is the slope of the pure  $a_i$  response curve as shown in Figs. 20 and 21.

Electrical potentials  $\Delta E_{ij}$  across both parchment supported membranes in the electrochemical cell of the type shown above were measured by taking fixed concentrations of both the primary ions (i.e.,  $i$  and  $j$ ) on the side (') and varying the concentration of the ionic species  $i$  and  $j$  on the side (") whereas in another experiment only one ion either  $i$  or  $j$  on the side (") at different concentration was taken and thus electrical potentials  $\Delta E_i$  or  $\Delta E_j$  were plotted against  $\log a_i$  or  $a_j$  as shown in Figs. 20 and 21. Parallel straight lines depicted in figures were obtained which

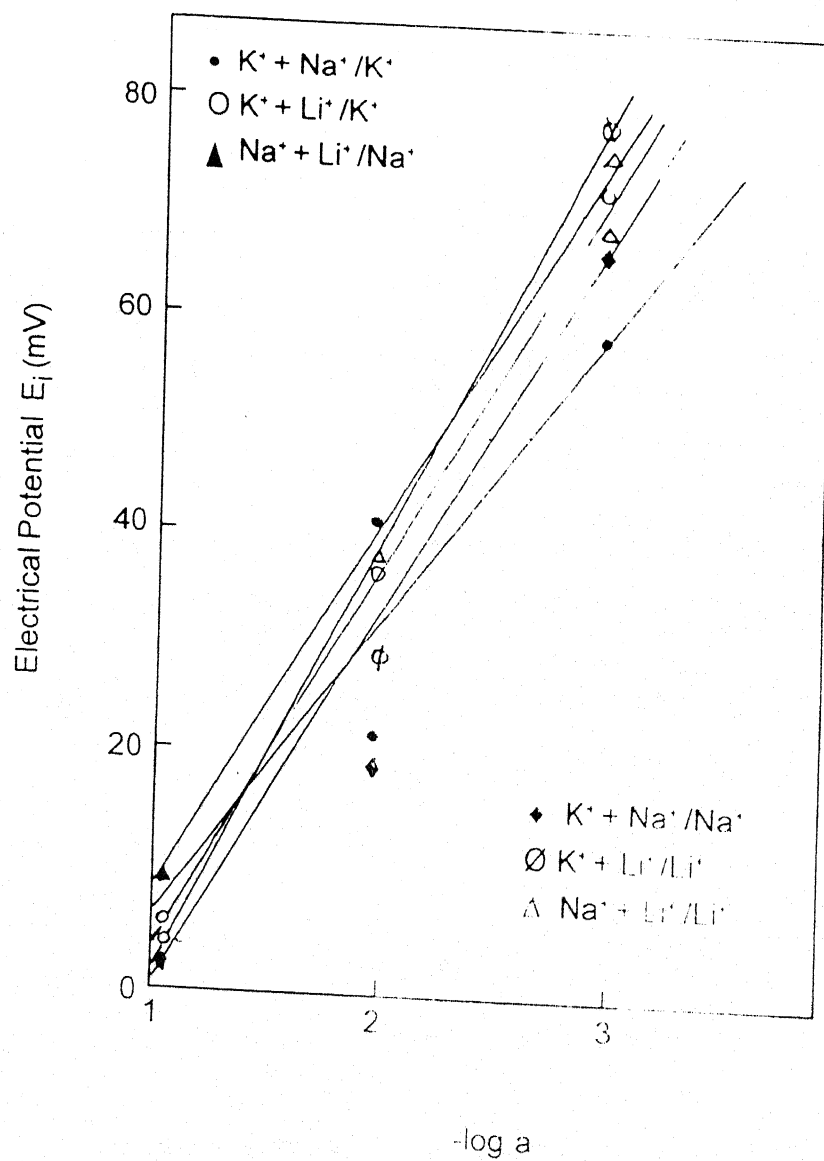


Fig. 20

Plots of Electrical potential  $E_i$  (mV) vs  $-\log a$  for nickel phosphate membrane.

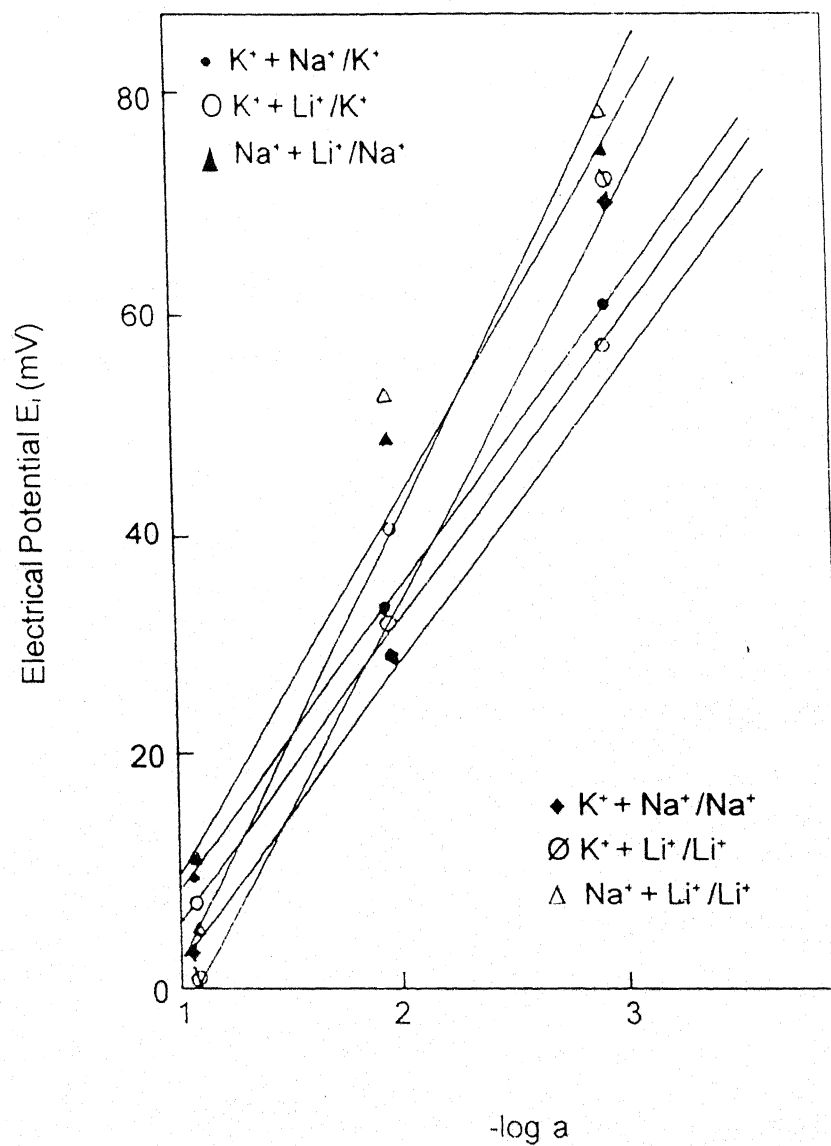


Fig 21

Plots of Electrical potential  $E_i$  (mV) vs. -log a for cobalt phosphate membrane.

indicates the ideal behaviour of the membranes systems. The slope  $S$  of the line was used to derive the values of  $K_{ij}^{\text{Pot}}$  (apparent) using eqn. (17). In this way, the values of the  $K_{ij}^{\text{Pot}}$  obtained for both the parchment supported nickel and cobalt phosphate membranes using various 1:1 electrolytes are given in Tables 17 and 18.

Parchment supported nickel and cobalt phosphate membranes in contact with various 1: 1 electrolyte solutions were thus considered as homogeneous membrane elements with charged rigid capillary structure or gels having a diameter large as compared to the thickness of the electrical double layer at the walls [9,10,14] in accordance with the classical fixed charge theory of Teorell [9], Meyer and Sievers [10], Schaep [51], Mohammad [52], Ariza [53], Kobatake and coworkers [54-57] and Tasaka and coworkers [33] etc. Flow of electrolyte by diffusion because of the presence of a net charge on the membrane gives rise to membrane potential which regulates the flow of electrolyte by increasing the speed of the slow moving ion and also by decreasing the speed of the fast moving ion. The electrical double layer at the membrane solution interface seems to control the ion permeation as suggested by Tien and Ting [58] for bilayer membranes and our findings with inorganic precipitate nickel and cobalt phosphate membranes. Perfect Donnan exclusion of coions was realized in the dilute limit of the external solution and that the selectivity sequence of the membranes for alkali metal ions was

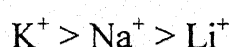


Table 18

Values of potentiometric selectivity constant ( $K_{ij}^{\text{Pot}}$ ) for the cobalt phosphate membrane at various electrolyte concentration.

Selectivity constant Concentration / Mol $l^{-1}$	$K_{K-Na}$	$K_{K-Li}$	$K_{Na-Li}$
$1 \times 10^{-1}$	0.82	0.49	0.60
$1 \times 10^{-2}$	1.10	1.20	1.40
$1 \times 10^{-3}$	3.50	4.01	3.20

### SELECTIVITY IN TERMS OF ENERGETIC TERMS :

In order to substantiate our findings and further to understand the selectivity of membranes in energetic terms, the values of various activation parameters have been evaluated on the basis of rate theory. The need for the use of rate theory has been felt because, electrical measurements carried out for assessing selectivity involve kinetic contributions to the permeation process and their explanation can not be expected to be given rigorously in terms of equilibrium energetics concepts. The rate theory describes any processes from diffusion to chemical reaction in terms of elementary jumps over energy barriers, and can be used to represent the processes of permeation in as much detail or with as much accuracy as desired. The permeant encounters energy maxima (barriers) and minima (wells) in its journey from one side of the membrane to the other. The energy maxima represents the energies of the transition states, and diffusion past these unfavourable loci that can be represented by single jumps over the corresponding barrier. The progress over each barrier is proportional to the number of ions attaining the energy needed to cross barrier. The rate constant  $K_i$  for crossing over a barrier is related to standard Gibb's Free energy of activation,  $\Delta F^*$ , by:

$$k_i = A_i \exp (-\Delta F^* / RT) \quad (18)$$

where  $A_i$  is the frequency of attempted hops. The  $\Delta F^*$  is related to enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) of activation:

$$\Delta F^* = \Delta H^* - T \Delta S^* \quad (19)$$

$\Delta H^*$  and  $\Delta S^*$  can be evaluated with the help of specific conductance,  $\pi$ , by making the use of the following relationship:

$$\pi = RT/Nh \exp (-\Delta H^*/RT) \exp (\Delta S^*/R) \quad (20)$$

The obtained values of  $\Delta H^*$  can be used to evaluate the Arrhenius activation energy,  $E_a$ , on the basis of the equation,

$$E_a = \Delta H^* + RT \quad (21)$$

To use equation (20),  $\log \pi nH / RT$  has been plotted against  $1/T$  as shown in Figs. 22 and 23. The straight line plots confirm the applicability of this equation to our model system and allow the calculation of  $\Delta H^*$  and  $\Delta S^*$  from the slopes and intercepts of the linear plots. The parameters so evaluated have been used to calculate the magnitude of  $\Delta F^*$  and  $E_a$  with the help of eqns. (19) and (21), respectively. The results of these calculations are summarized in Tables 19 and 20.



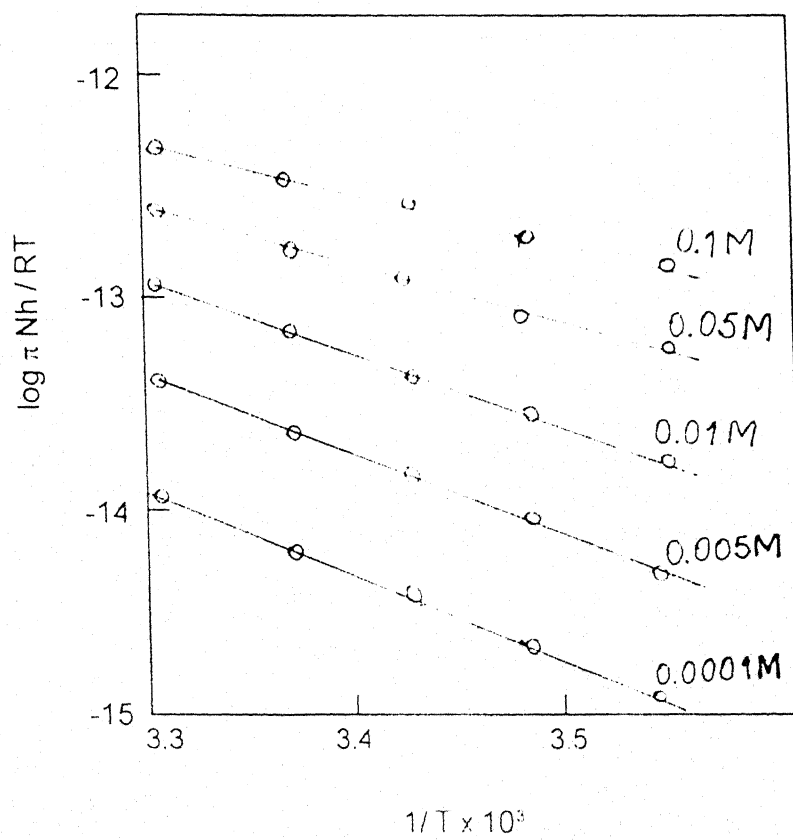


Fig. 22

Plots of  $\log \pi N_h / RT$  vs  $1/T$  for nickel phosphate membrane.

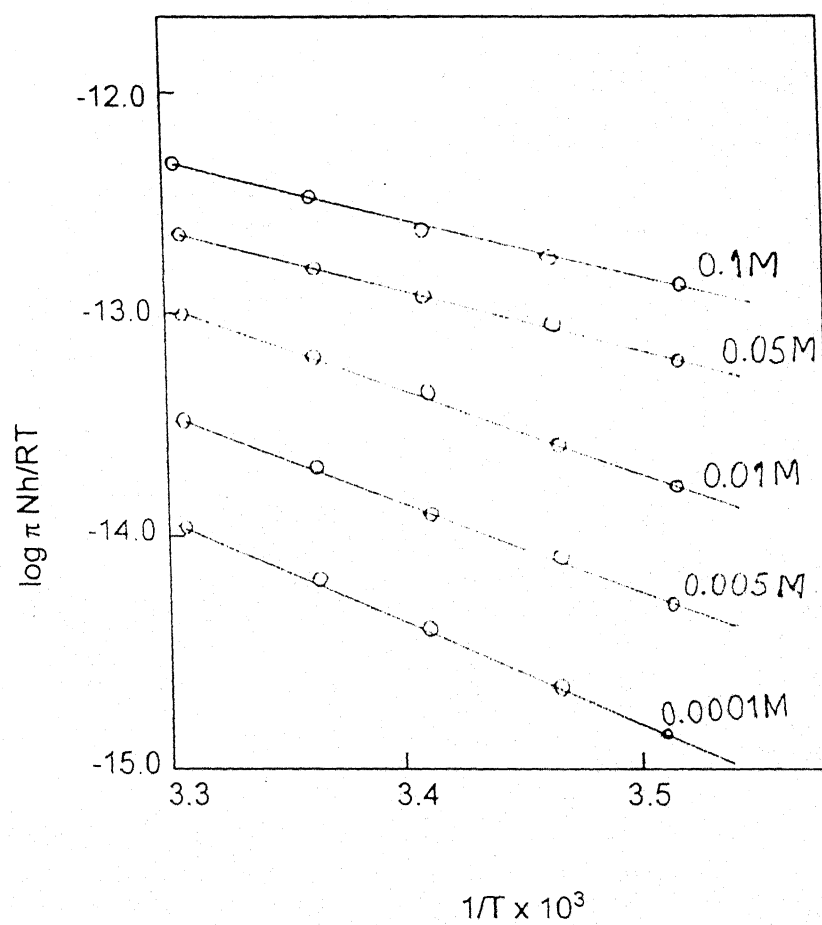


Fig 23

Plots of  $\log \pi Nh/RT$  vs.  $1/T$  for  
cobalt phosphate membrane.

Table 19

The values of thermodynamic activation parameters evaluated on the basis of theory of absolute reaction rates.

Membrane	Nickel Phosphate				
Electrolyte	Concentration n	$E_a$	$\Delta F^*$	$\Delta H^*$	$-\Delta S^*$
KCl	$1 \times 10^{-1}$	1.30	10.80	1.32	14.30
	$5 \times 10^{-2}$	2.10	13.65	2.75	15.21
	$1 \times 10^{-2}$	4.11	15.92	3.90	16.70
	$5 \times 10^{-3}$	5.65	17.10	5.25	17.50
	$1 \times 10^{-3}$	7.10	18.75	6.50	20.70
NaCl	$1 \times 10^{-1}$	1.13	11.8	1.11	19.20
	$5 \times 10^{-2}$	2.94	13.27	2.17	19.82
	$1 \times 10^{-2}$	4.17	15.22	3.32	20.16
	$5 \times 10^{-3}$	5.35	17.23	4.97	21.37
	$1 \times 10^{-3}$	6.94	18.24	6.23	23.13
LiCl	$1 \times 10^{-1}$	1.01	11.60	1.01	20.0
	$5 \times 10^{-2}$	2.91	11.13	2.73	21.32
	$1 \times 10^{-2}$	4.13	15.53	3.50	22.75
	$5 \times 10^{-3}$	5.23	17.14	4.75	23.35
	$1 \times 10^{-3}$	6.17	17.43	9.97	24.25

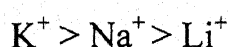
Table 20

The values of thermodynamic activation parameters evaluated on the basis of theory of absolute reaction rates.

Membrane	Cobalt Phosphate				
Electrolyte	Concentratio n	E <sub>a</sub>	ΔF*	ΔH*	- ΔS*
KCl	1x10 <sup>-1</sup>	1.50	11.0	1.37	14.0
	5x10 <sup>-2</sup>	2.40	13.72	2.81	15.14
	1x10 <sup>-2</sup>	4.15	15.98	3.96	16.63
	5x10 <sup>-3</sup>	5.71	17.23	5.32	17.08
	1x10 <sup>-3</sup>	7.40	18.82	6.80	20.63
NaCl	1x10 <sup>-1</sup>	1.21	11.3	1.16	17.5
	5x10 <sup>-2</sup>	2.98	13.32	2.25	18.22
	1x10 <sup>-2</sup>	4.23	15.41	3.42	19.34
	5x10 <sup>-3</sup>	5.41	17.36	5.13	20.45
	1x10 <sup>-3</sup>	6.70	18.27	6.10	21.37
LiCl	1x10 <sup>-1</sup>	1.01	11.80	1.07	20.20
	5x10 <sup>-2</sup>	2.98	11.19	2.84	21.41
	1x10 <sup>-2</sup>	4.27	15.67	3.76	22.87
	5x10 <sup>-3</sup>	5.63	17.28	4.88	23.52
	1x10 <sup>-3</sup>	6.38	18.83	9.96	24.45

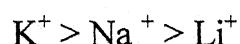
The size dependence of the magnitude of  $E_a$ ,  $\Delta F^*$  and  $\Delta H^*$  shows that a larger ion has more difficulty in crossing the membrane than a smaller one. This type of variation can be explained by considering the location of energy peaks and wells and also by comparing the heights of energy barriers (i.e., the difference between outer wells and peaks). It has been found that the larger ion encounters a bigger entrance barrier lying very close to the surface of the membrane. The entrance barrier for the smaller ion is not only to lesser height but also lies farther in [26]. The location of the outermost well has been assumed to be the same for all the species, while that of the inner well is much farther in for the smaller ion than the larger ones. Keeping in mind these facts, it can be argued that the magnitude of the above mentioned activation parameters should be higher for larger ions than for smaller ones.

The magnitude of  $\Delta S^*$  indicates the mechanism of flow, and has been interpreted in a number of ways. The low negative values of  $\Delta S^*$  found for ion permeation through the parchment membrane used in the present investigation are attributable to electrolyte diffusion with partial immobilization in the membrane, the partial immobility increasing with the increase of density of charge on the permeant. This conclusion is in good agreement with the most recent findings of Marcus [59], who established that the translational immobilization entropy of solvents follows the sequence  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  resulting the selectivity sequence of the membranes for alkali metal ions as:



## CONCLUSION

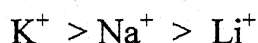
The parchment supported inorganic precipitated nickel and cobalt phosphate membranes which are used as the model membranes have been studied thoroughly for their selectivity to the metal ions. Initially their effective charge densities were evaluated using the practically observed values of electrical membrane potential and also others thermodynamic parameters like selectivity and transference number in order to find the membrane selectivity of metal ions. This on the basis of these results the selectivity order of metal ions for both the membranes was obtained



Further, to substantiate the finding of selectivity sequence, various methods; (a) Biionic method: interposing the membrane between two electrolyte of same concentration and on the other hand by varying the concentration of an electrolyte on one side and keeping of other constant; (b) Mixture Method: in which the solutions of the mixture of two electrolytes at a time were separated by the membranes were employed. After having observed the biionic potential values across both the membranes experimentally along with the electrical membrane conductance and applying the various recently developed theories of membrane selectivity, on these observations the above order of the

selectivity was confirmed. In this way the author has characterised both the membranes for the selectivity of the metal ions using effective fixed charge density, biionic potential and conductivity measurements.

In the last a major advancement towards membrane selectivity on the behalf of recently developed theory in that equilibrium selectivity among alkali metal cations could also be explained in energetic terms, as the differences in Gibb's free energy lost in dehydrating the ions and that gained by integration with binding sites. In this way the selective membrane behavior in terms of thermodynamic activation parameters evaluated, utilizing the theory of absolute reaction rate was also found the same:



The size dependence of the magnitude of various thermodynamic activation parameters show that the larger ion, which faces a bigger entrance barrier lying very close to the surface of the membrane, has more difficulty in crossing the membrane than the smaller ions, for which the entrance barrier is not only lower but also lies further in. The low negative values of entropy of activation are an indication of the fact that electrolyte diffusion takes place with partial immobility immobilization in the membrane. The partial immobility following the order of density of charge on the permanent.

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Chapter-IV

**BI-IONIC POTENTIAL STUDIES**

## Chapter -IV

### INTRODUCTION

An ion exchange membrane separating two electrolyte solutions maintains across itself an electric potential difference, which can be measured with suitable electrodes. Potentials between solutions of the same electrolyte but of different concentrations are customarily defined as concentration potentials, and those between solutions of different electrolytes but of equal concentration as bi-ionic potentials. These bi-ionic potentials (BIP) are of great interest in biology and acquire increasing interest in industrial practice.

Most probably first time the bi-ionic potential values were reported by Marshall et al. (1), Meyer and Bernfield (2), Sullener et al. (3,4) Manacle (5), and Wyllie (6) using the Henderson equation for liquid junction potential (7) and replacing the concentrations by activities, Marshall (1) derived equations for the bi-ionic membrane potential theories in order to characterise the membranes as well as to test these membrane as well as to bi-ionic potential theories. Under the studies of bi-ionic potential and confrontation with experimental results, L. Dammak and co-workers (14) carried out the theoretical study of bi-ionic potential (BIP) in the case of mixed control of the inter-diffusion process and compared with experimental results in order to test the theories. Recently a no of investigators (15-17) have also utilized (BIP) membrane potential theories

for characterizing the various types of the membranes with a view to establish their applications.

The mechanism of the bi-ionic potential was considered in detail by Sollner (3,4). He found that not only the relative mobility of the counter-ions was important but also the selectivity of the membrane material equally played significant role. According to his views, when the membrane is fixed in a bi-ionic cell, one ion is preferred to the same extent as the membrane is in equilibrated with mixed solution containing both counter-ions. His equation for the potential (restricted to 1:1 electrolytes),

$$\Delta\phi = \frac{RT}{F} \ln \frac{\bar{D}_A \bar{V}_B}{\bar{D}_B \bar{V}_A} \quad (1)$$

reflects the two factors relative to mobility  $(\bar{D}_A / \bar{D}_B)$  and preferential adsorption  $(\bar{V}_B / \bar{V}_A)$  by the membrane.

Wyllie (6) combines the theories of Sollner and Marshall and uses the Henderson equation (with activities) for the diffusion potential in the membrane. He also adds the Donnan potentials, and, as Sollner corrects for the assumed preferential adsorption by multiplying the mobility ratio with the activity coefficient ratio. His equations are, as Eqn. 1, in accordance with those derived quasi thermodynamically.

Recently, Toyoshima et al. (18-22) have derived various equations for bi-ionic potential and membrane potential on the basis of non equilibrium thermodynamics, using the appropriate assumptions for the mobilities and activity coefficients of small ions in the membrane phase. The theory is applied and tested here for the nickel phosphate and cobalt

phosphate membrane respectively. The salient features of Toyoshima et al. (22) theory are described below.

Consider a system in which two large compartments contain aqueous solutions composed of two simple 1:1 electrolyte AP and BP. here A and B represent the cationic species and P is the common anion. The system is isothermal and there is no electric field applied externally across the membrane. The electric charge carried by the membrane matrix is negative  $\theta$ . The solutions are so vigorously stirred that the concentration in each of the compartments is maintained uniformly. The flow of all components in the membrane is considered to occur only in the direction of membrane is considered to occur only in the direction of membrane thickness. Neglecting interacting flows between ions of different species and the effect of mass flows, the fluxes of ions A, B and P are give by

$$T_N = -\mu_N (RT d \ln a_N / dx + F d\phi / dx). \quad (2)$$

$$(N=A,B)$$

$$J_p = -\mu_N C_p (RT d \ln a_p / dx + F d\phi / dx) \quad (3)$$

Where  $J_i$  ( $i = A,B,P$ ) is the flux of ionic species, I relative to the frame of reference fixed to the membrane,  $U_i$ ,  $C_i$  and  $A_i$  are the mobility (relative to the local centre of mass), molar concentration and activity of ion I. For the unidimensional flows, the law of mass conservation gives the equation.

$$dJ_i / dx = 0 \quad (i=A,B,P) \quad (4)$$



when the flows are stationary. Hence we have  $J_n = \text{constant}$  with respect to axial direction. Rearranging the equation 3, the gradient of the electrochemical potential of the anion is represented in terms of  $J_p$ ,  $A_p$  and  $C_p$  as

$$\frac{d\mu_p}{dx} = RT d \ln a_a dx - F d\phi / dx = -J_p / u_p c_p \quad (5)$$

The integration of Eqn. 5 between two bulk solutions across the membrane leads to

$$\Delta u_p = -J_p \int_0^l (1 / u_p c_p) dx = -F \Delta \phi RT \ln(a_p^{II} / a_p^I) \quad (6)$$

where I and II indicate the values in the external solutions 1 and 2 and  $\Delta \phi$  is the difference of the electric potential between two bulk solutions. Then  $\theta_{II}$  and  $\theta_I$  is the BIP. Using the steady state conditions,  $J_p = \text{constant}$  with respect to  $x$ , eqn. 6 may be written to give

$$\Delta \phi BIP = (j_p / F) \int_0^l (1 / u_p c_p) dx + \left( \frac{RT}{F} \right) \ln(a_p^{II} / a_p^I) \quad (7)$$

In the system of negatively ionizable membrane and a 1:1 electrolyte the following assumptions are made for the concentration of  $u_i$  and  $a_i$  of ion  $i$  ( $i = +, -$ ) in the membrane phase (22)

$$u^+ C_+ = u^0 + (\underline{C} + \theta) \quad (8)$$

$$u_- c_- = u_-^0 c_-$$

$$a_+ = v^0 + (\underline{C} + \theta)$$

$$a_- = \underline{v}^0 \underline{C} \quad (9)$$

Here  $u_i^0$  and  $v_i^0$  are the mobility and activity coefficient of ion  $i$  in free solution. The quantity  $\theta$  is called the thermodynamically effective concentration of counter ions dissociated from the ionizable groups fixed on membrane matrix.

The system is now composed of the following four kinds of electrolytes AP, BP, AM and BM, where M represents the negatively ionizable group fixed on the membrane skeleton. The Eqns. 8 and 9 are applied to the system with the following assumption (22). The ratio of  $C_{AM}$  to  $C_{BM}$  is equal to that of  $C_{AP}$  to  $C_{BP}$ , i.e.,

$$\frac{C_{AM}}{C_{BM}} = \frac{C_{AP}}{C_{BP}} \quad (10)$$

and electrical neutrality is main in any element of the membrane, so

$$C_{AM} + C_{BP} = \theta \quad (11)$$

The expressions for the activities and the motilities for small ions in the membrane under above stated conditions are given by following expressions,

$$a_A = C_{AP} [1 + \theta / (C_{AP} + C_{BP})] \quad (12)$$

$$a_B = C_{BP} [1 + \theta / (C_{AP} + C_{BP})]$$

$$a_P = C_{AP} + C_{BP}$$

$$u_A C_A = u_A^0 a_A$$

$$u_B C_B = u_B^0 a_B \quad (13)$$

$$u_P C_P = U^0 P a_P$$

Where  $C_{AP}$ ,  $C_{BP}$ ,  $C_{AM}$  and  $C_{BM}$  are the concentrations of the electrolytes AP, BP AM and BM respectively.

Equation 7, for the bi-ionic potential may be rewritten in the following form

$$\Delta\phi_{BIP} = \left( \frac{RT}{F} \right) \left( \frac{\epsilon_L + \eta_L - 1}{\epsilon_0 + \eta_0 - 1} \right) (2j-1)x \quad (14)$$

$$\ln \left( \frac{\epsilon_L + \eta_L - 1}{\epsilon_0 + \eta_0 - 1} \right)$$

where  $\epsilon_0$  and  $\epsilon_L$  are the values of  $\epsilon$  in the membrane phase at  $x=0$  and  $x=L$  and  $\eta_0$  and  $\eta_L$  are the corresponding values of  $\eta$ . The term  $\epsilon$  and  $\eta$  are the reduced concentrations defined by  $\epsilon = (C_{AP}/\theta) + C_{AP}/(C_{AP} + C_{BP})$

By taking the assumption, that at both membrane surfaces the equilibrium distribution of every ion species is maintained between the membrane phase and external bulk solution (22) and also neglecting the effect of osmotic pressure produced between the two phases, the following expression are obtained.

$$\begin{aligned} K_N^2 (a_{NP})_I^2 &= (a_N)O(a_P)_0 \\ K_N^2 (a_{NP})_{II}^2 &= (a_N)L(a_P)_L \end{aligned} \quad (15)$$

where  $(a_{NP})_I$  and  $(a_{NP})_{II}$  are the mean activities of the electrolytes NP ( $N=A, B$ ) in both solutions I and II respectively, defined by

$$\begin{aligned} (a_{BP})_I^2 &= a_N^I a_P^I \\ (a_{BP})_{II}^2 &= a_N^{II} a_P^{II} \end{aligned} \quad (16)$$

$(a_i)_0$  and  $(a_i)_L$ , ( $i=A, B, P$ ) are the single ion activities of species in the membrane phase at  $x=0$  and  $x=L$  and  $K_N$  ( $N=A, B$ ) is defined by

$$1/K_N = \exp[\mu_N^{um} - \mu_N^{om} + \mu_P^{om} - \mu_P^{oh} / 2RT] \quad (17)$$

In Eqn. 17,  $\mu^0 N^m$  is the standard chemical potential of cation in the membrane phase and  $\mu^0 N^h$  is that in external bulk solution and  $\mu^0 P^M$  and  $\mu^0 P^B$  are the corresponding values of anion P.

By solving various equations, Toyoshima et al (22) gave the equation for BIP in the following form

$$\Delta\phi_{BIP} = \left[ 21n \left( \frac{K_A}{K_B} \right) = \ln \left( \frac{JV_A + 1}{JV_B + 1} \right) \right] (F / RT) \quad (18)$$

This equation is used for the determination of theoretical values of BIP for nickel and cobalt phosphate membrane respectively.

## **EXPERIMENTAL**

### ***Preparation of Membrane :***

Parchment supported membrane of nickel phosphate and cobalt phosphate were fabricated by the method of interaction suggested by Kushwaha and co-worker as shown in chapter third of the thesis. For the preparation of these membranes nickel (II) chloride and cobalt (III) chloride were used separately with trisodium orthophosphate and parchment paper. The membrane thus prepared were washed with deionized water to remove the free electrolyte and were found to give quite reproducible results of membrane potential and bi-ionic potential.

## Measurement of Membrane Potential and Bi-ionic Potential

The electrochemical cell of the type

	Solution		Solution	
Ag-AgCl	C <sub>1</sub>	Membrane	C <sub>2</sub>	AgCl-Ag

was used for measuring electrical potentials arising across the membranes by maintaining a ten - fold difference in concentration ( $C_2/C_1=10$ ) and using a Pye Precision Vernier potentiometer (No. 7568). The bi-ionic potential were determined by setting up an electrochemical cell of the following type and keeping the concentration of both Ap and Bp electrolytes to be the same. The various salt solutions (Chloride of Li<sup>+</sup> Na<sup>+</sup> and K<sup>+</sup>) were prepared from analytical grade reagents (B.D.H.) by using deionized water. In both the measurements of membrane potential and bi-ionic potential the solution were vigorously stirred temperature was maintained at 25°C.

	Solution		Solution	
Ag-AgCl	AP	Membrane	BP	AgCl-Ag

and keeping the concentration of both Ap and Bp electrolytes to be the same. The various salt solutions (Chloride of Li<sup>+</sup> Na<sup>+</sup> and K<sup>+</sup>) were prepared from analytical grade reagents (B.D.H.) by using deionized water. In both the measurements of membrane potential and bi-ionic potential the solutions were vigorously stirred and temperature was maintained at 25°C.

## RESULT AND DISCUSSION

Michaelis (23) derived a relation between the BIP and selectivity, which is

$$\text{given by } \Delta\phi_{BIP} = \frac{RT}{F} \ln(\bar{\mu}_i / \bar{\mu}_j) \quad (1)$$

Where  $\bar{\mu}_i$  and  $\bar{\mu}_j$  are the mobilities of the permeating ions.

Marshall and Krinbill (1) expressed the potential as a function of the products of mobilities and activities as :

$$\Delta\phi_{BIP} = (RT / F) \ln(a_i \bar{\mu}_i / a_j \bar{\mu}_j) \quad (2)$$

Wyllie (6) considered the selectivity that the membrane would exert on ions and derived for the BIP an equation similar to Eqn. 2 His expression for the BIP (6,24) is given by

$$\Delta\phi_{BIP} = (RT / F) \ln(a_i / a_j) (\bar{\mu}_i / \bar{\mu}_j) \quad (3)$$

and intramembrane mobility rates is expressed by

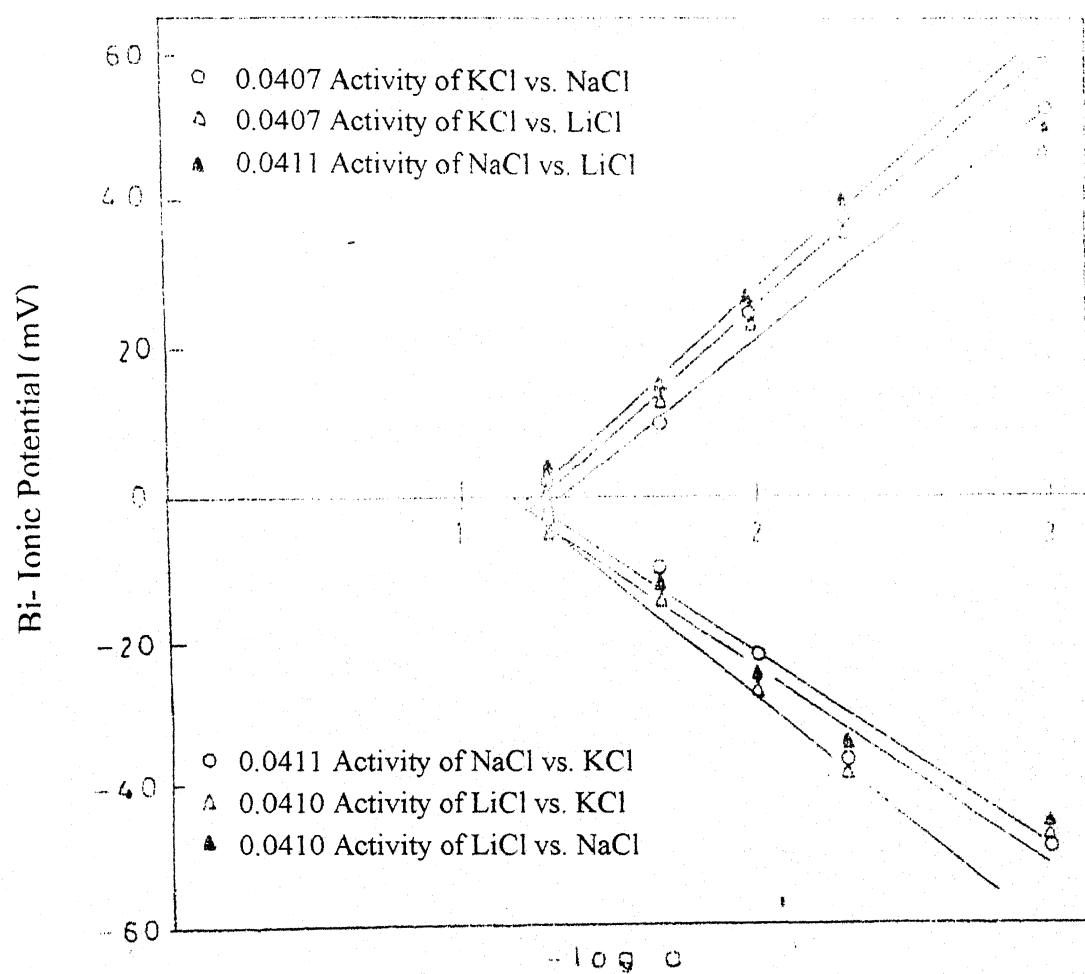
$$\bar{\mu}_i / \bar{\mu}_j = \bar{t}_i / \bar{t}_j = (\bar{m}_i / \bar{m}_j) (\bar{\lambda}_i / \bar{\lambda}_j) \quad (4)$$

where  $\bar{t}_i / \bar{t}_j$  is the intramembrane transference ratio,  $\bar{m}_i$  and  $\bar{m}_j$  are the steady state equilibrium concentration of i and j in the respective zone,  $\bar{\lambda}_i$  is the conductivity of the membrane when it is wholly in i form and  $\bar{\lambda}_j$  is the conductivity of the membrane when it is wholly in j form.

The quantity  $\bar{\mu}_i / \bar{\mu}_j$  is considered truly a membrane property (25). It is independent of the changes made in the activities  $a_i$  and  $a_j$  of the external solution. Thus it is apparent from Eqn. 2 that a plot of  $\log a_i$  against

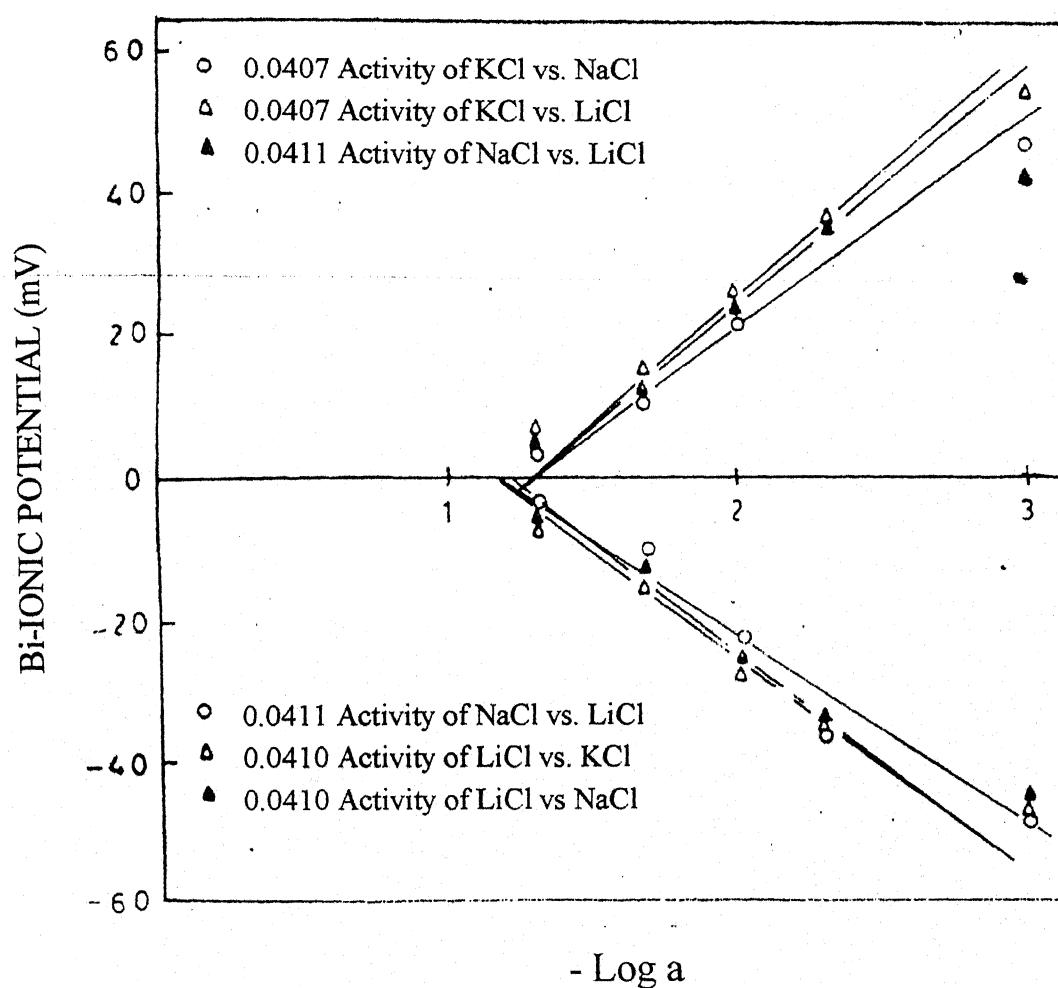
potential for a constant  $a_j$  should give a straight line. Similarly a straight line should be obtained if  $a_j$  is varied and  $a_i$  is kept constant.

Bi-ionic potential developed by nicked phosphate and cobalt phosphate membrane were determined for various electrolyte pairs, viz., KCL-NaCL, KCL-LiCl and NaCl-LiCl taking the concentration of one of the electrolyte constant (0.05 mol/l) and varying the concentration of the other electrolyte between 0.001 mol/l to 0.05 mol/l. In the second set of experiment the concentration of the other electrolyte was kept constant (0.05 mol/l) and the concentration of the first electrolyte was varied. The bi-ionic potentials thus observed were plotted against logarithm of the activity. Two set of straight lines in accordance with the expectation of Eqn. 2, are obtained and are shown in Figures 1 and 2. The straight lines confirm the earlier view of Wyllie and Kanaan (6, 25) that the intramembrane mobility ratio  $\bar{\mu}_i/\bar{\mu}_j$  remains constant irrespective of the concentrations of the electrolyte across the membranes. In order to derive the values of the intramembrane mobility ratio, these straight lines were extended to cut the activity axis at zero potential. Thus two sets of  $a_i$  and  $a_j$  values for which bi-ionic potential was zero, to  $\bar{\mu}_i/\bar{\mu}_j$ . The values of  $\bar{\mu}_i/\bar{\mu}_j$  derived in this way for different electrolyte pairs are  $\bar{\mu}_{K^+}/\bar{\mu}_{Na^+} = 1.04, \bar{\mu}_{K^+}/\bar{\mu}_{Li^+} = 1.30, \bar{\mu}_{Na^+}/\bar{\mu}_{Li^+} = 1.29$  for nickel phosphate and  $\bar{\mu}_{K^+}/\bar{\mu}_{Na^+} = 1.23, \bar{\mu}_{K^+}/\bar{\mu}_{Li^+} = 1.30, \bar{\mu}_{Na^+}/\bar{\mu}_{Li^+} = 1.22$  for cobalt phosphate membrane.



**Fig.1** PLOT OF Bi-IONIC POTENTIAL AGAINST  $-\log a$  FOR VARIOUS PAIRS OF ELECTROLYTES WITH NICKEL PHOSPHATE MEMBRANE





**Fig. 2** PLOTS OF BI-IONIC POTENTIAL AGAINST  $\log a$  FOR VARIOUS PAIRS OF ELECTROLYTES WITH COBALT PHOSPHATE MEMBRANE.

Bi-ionic potential measurements were also carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The values of bi-ionic potentials across parchment supported nickel phosphate and cobalt phosphate membranes with various 1:1 electrolyte combinations at different concentrations are given in Tables 1 and 2. Equation 2 was used to calculate the intramembranes mobility ratio  $\bar{\mu}_i/\bar{\mu}_j$ . The values of  $\bar{\mu}_i/\bar{\mu}_j$  thus calculated for both the membrane are given in Table 3 and 4. An interesting point with the value of  $\bar{\mu}_i/\bar{\mu}_j$  is the fact that the mobility ratio goes through a considerable change with the concentration of external solutions. This behavior is seen with both the membranes and different electrolyte pairs.

The theoretical values of BIP can be obtained using the following reactions given by toyoshima et. al.

$$\Delta\phi_{BIP} = \left[ 21n \left( \frac{K_A}{K_B} \right) = \ln \left( \frac{JV_B + 1}{JV_B + 1} \right) \right] (F / RT) \quad (5)$$

J can be calculated from the relation

$$(2j+1) \ln \left( \frac{g_A + 2J}{g_B + 2J} \right) - \ln \left( \frac{JV_B + 1}{JV_B} \right) - \ln \left( \frac{g_A}{g_B} \right) = 0 \quad (6)$$

$$\text{where } V_N = 1 + (\mu_N^0 / \mu_P^0) \quad (7)$$

$$\text{and } g_N = 1 + \left[ 1 + \left( \frac{2K_N C}{\theta} \right) \right]^{1/2} \quad (8)$$

Knowing the values of parameter  $K_A$ ,  $K_B$ ,  $\theta$ ,  $V_A$  and  $V_B$ , the values of theoretical  $\Delta\phi_{BIP}$  can be calculated from Eqn. 5. For the evaluation of

**Table 1**

Observed bi-ionic potential at  $25 \pm 0.1^\circ\text{C}$  across nickel phosphate membrane in contact with various 1:1 electrolyte pair at same concentration.

<b>Electrolyte Pairs Concentrations (mol/l)</b>	<b>KCl-NaCl (mV)</b>	<b>KCl-LiCl (mV)</b>	<b>NaCl-LiCl (mV)</b>
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.26	-3.94	-2.26
$5 \times 10^{-2} / 5 \times 10^{-2}$	4.54	-2.74	-2.03
$2 \times 10^{-2} / 2 \times 10^{-2}$	6.75	1.54	1.45
$1 \times 10^{-2} / 1 \times 10^{-2}$	8.57	2.60	2.24
$5 \times 10^{-3} / 2 \times 10^{-3}$	11.65	3.45	4.15
$1 \times 10^{-3} / 1 \times 10^{-3}$	19.85	16.00	13.46

**Table 2**

Observed bi-ionic potential at  $25 \pm 0.1^\circ\text{C}$  across nickel phosphate membrane in contact with various 1:1 electrolyte pair at same concentration.

<b>Electrolyte Pairs Concentrations (mol/l)</b>	<b>KCl-NaCl (mV)</b>	<b>KCl-LiCl (mV)</b>	<b>NaCl-LiCl (mV)</b>
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.41	-4.52	-4.21
$5 \times 10^{-2} / 5 \times 10^{-2}$	2.55	-2.46	-2.46
$2 \times 10^{-2} / 2 \times 10^{-2}$	4.45	1.65	-1.15
$1 \times 10^{-2} / 1 \times 10^{-2}$	6.80	2.62	0.99
$5 \times 10^{-3} / 2 \times 10^{-3}$	13.30	5.11	3.45
$1 \times 10^{-3} / 1 \times 10^{-3}$	14.80	18.50	9.76

**Table 3**

Values of the intramembrane mobility ratio of various 1:1 electrolyte ion pairs across nickel phosphate membrane at same concentrations.

<b>Electrolyte Pairs Concentrations (mol/l)</b>	$\bar{\mu}_{K^+} / \bar{\mu}_{Na^+}$	$\bar{\mu}_{K^+} / \bar{\mu}_{Li^+}$	$\bar{\mu}_{Na^+} / \bar{\mu}_{Li^+}$
1x10 <sup>-1</sup> /1x10 <sup>-1</sup>	1.07	1.06	1.09
5x10 <sup>-2</sup> /5x10 <sup>-2</sup>	1.09	1.07	1.15
2x10 <sup>-2</sup> /2x10 <sup>-2</sup>	1.24	1.20	1.25
1x10 <sup>-2</sup> /1x10 <sup>-2</sup>	1.43	1.48	1.35
5x10 <sup>-3</sup> /2x10 <sup>-3</sup>	1.55	1.70	1.48
1x10 <sup>-3</sup> /1x10 <sup>-3</sup>	1.77	1.84	1.67

**Table 4**

Values of the intramembrane mobility ratio of various 1:1 electrolyte ion pairs across cobalt phosphate membrane at same concentrations.

<b>Electrolyte Pairs Concentrations (mol/l)</b>	$\mu_{K^+} / \mu_{Na^+}$	$\mu_{K^+} / \mu_{Li^+}$	$\mu_{Na^+} / \mu_{Li^+}$
$1 \times 10^{-1} / 1 \times 10^{-1}$	1.13	1.19	1.09
$5 \times 10^{-2} / 5 \times 10^{-2}$	1.19	1.33	1.21
$2 \times 10^{-2} / 2 \times 10^{-2}$	1.30	1.46	1.30
$1 \times 10^{-2} / 1 \times 10^{-2}$	1.46	1.62	1.47
$5 \times 10^{-3} / 2 \times 10^{-3}$	1.50	1.66	1.54
$1 \times 10^{-3} / 1 \times 10^{-3}$	1.82	1.72	1.60

these parameters, separate experiments for membrane potential were carried out.

According to Toyoshima (22) the value of membrane potential  $\Delta\phi_{BIP}$  arising between two solutions of the same electrolyte but of different concentrations  $C_N^I$  and  $C_N^{II}$  separated by a (negatively) ionizable membrane is given by

$$\left(\frac{F}{RT}\right)\Delta\phi_m = -\ln\delta - (1 - 2/V_N)x$$

$$\ln \frac{\sqrt{1 + (20_N^{II} K_N / \theta)^2 + (1 - 2/V_N)}}{\sqrt{1 + (20_N^I K_N / \theta)^2 + (1 - 2/V_N)}} \quad (9)$$

$$+ \ln \frac{\sqrt{1 + (20_N^I K_N / \theta)^2 + 1}}{\sqrt{1 + (20_N^{II} K_N / \theta)^2 + 1}}$$

where  $\delta = C_N^{II} / C_N^I$  Expansion of Eqn. 9 in powers of  $(1/C_N^{II})$  with the concentration ratio  $\delta = 10$  being kept constant yields.

$$\left(\frac{F}{RT}\right)\Delta\phi_m = -(1 - 2/V_N)\ln\delta - 2(1 - 1/V_N)(1/V_N)(1/V_N)x$$

$$(1 - 1/\delta)\left(\frac{\theta}{K_N}\right)(1/C_N^{II}) + \dots \quad (10)$$

The apparent transference number  $t_-$  for co-ion species, is defined by Ernst equation.

$$\left(\frac{F}{RT}\right)\Delta\theta_m = -(1 - 2t_-)\ln\delta. \quad (11)$$

Introducing Eqn. 10 into Eqn. 11 and expanding  $1/t_-$  as a power series in  $1/C_N''$  the following expression is obtained.

$$\frac{1}{t_-} = V_N + (V_N - 1) \left[ \frac{\delta - 1}{\delta \ln \delta} \right] x \left( \frac{\theta}{K_N} \right) (1 - C_N'') \quad (12)$$

From this equation, the values of  $V_N$  and  $\theta/K_N$  can be determined from the ordinate intercept and initial slope of a plot for  $1/t_-$  against  $1/C_N''$  at a given  $\delta = 10$

The membrane potential data obtained with each of the two types of parchment supported membrane namely (A) nickel phosphate and (B) cobalt phosphate, using various 1:1 electrolytes, are plotted as a function of  $\log (C_1 + C_2/2)$  with the ratio  $\delta (= C_2/C_1)$  fixed at 10. These values are given in Tables 5 and 6 and the plots are shown in figure 3.

Equation 12 indicates that the intercept of a plot of  $1/t_-$  against  $1/C_N''$  at fixed  $\delta = 10$  allows the values of  $V_N$  to be determined. The values of  $t_-$  is calculated from Eqn. 11 for both members and are given in Tables 7 and 8. Plots of  $1/t_-$  against  $1/C_N''$  for various 1:1 electrolytes are shown in Figure 4, for both nickel phosphate and cobalt phosphate membrane. For the evaluation of  $(\theta/K_N)$  the slope of Eqn. 12. which is given by the following is first determined.

$$(V_N - 1) \left[ (\delta - 1) / \delta \ln \delta \right] (\theta / K_N)$$

The graphical value of the slope determined from Figure 4, is equated with the above expression and then substituting  $V_N$  in it, the value of  $(\theta/K_N)$  is



Table 5

Observed membrane potential at  $25 \pm 0.1^\circ\text{C}$  across nickel phosphate membrane in contact with various 1:1 electrolyte at different concentration.

Electrolyte Pairs Concentrations (mol/l)	KCl-NaCl (mV)	KCl-LiCl (mV)	NaCl-LiCl (mV)
$1 \times 10^{-1} / 1 \times 10^{-1}$	3.46	4.46	4.87
$5 \times 10^{-2} / 5 \times 10^{-2}$	9.13	7.77	6.31
$2 \times 10^{-2} / 2 \times 10^{-2}$	25.81	22.32	15.77
$1 \times 10^{-2} / 1 \times 10^{-2}$	32.72	28.19	24.81
$5 \times 10^{-3} / 2 \times 10^{-3}$	46.72	42.66	37.77
$1 \times 10^{-3} / 1 \times 10^{-3}$	49.66	48.88	43.32

**Table 6**

Observed membrane potential at  $25 \pm 0.1^\circ\text{C}$  across cobalt phosphate membrane in contact with various 1:1 electrolyte at different concentration.

<b>Electrolyte Pairs Concentrations (mol/l)</b>	<b>KCl-NaCl (mV)</b>	<b>KCl-LiCl (mV)</b>	<b>NaCl-LiCl (mV)</b>
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.31	1.25	-2.00
$5 \times 10^{-2} / 5 \times 10^{-2}$	5.11	3.00	5.11
$2 \times 10^{-2} / 2 \times 10^{-2}$	15.67	11.33	14.30
$1 \times 10^{-2} / 1 \times 10^{-2}$	22.10	17.10	20.12
$5 \times 10^{-3} / 2 \times 10^{-3}$	31.11	34.12	3.00
$1 \times 10^{-3} / 1 \times 10^{-3}$	38.10	40.11	35.00

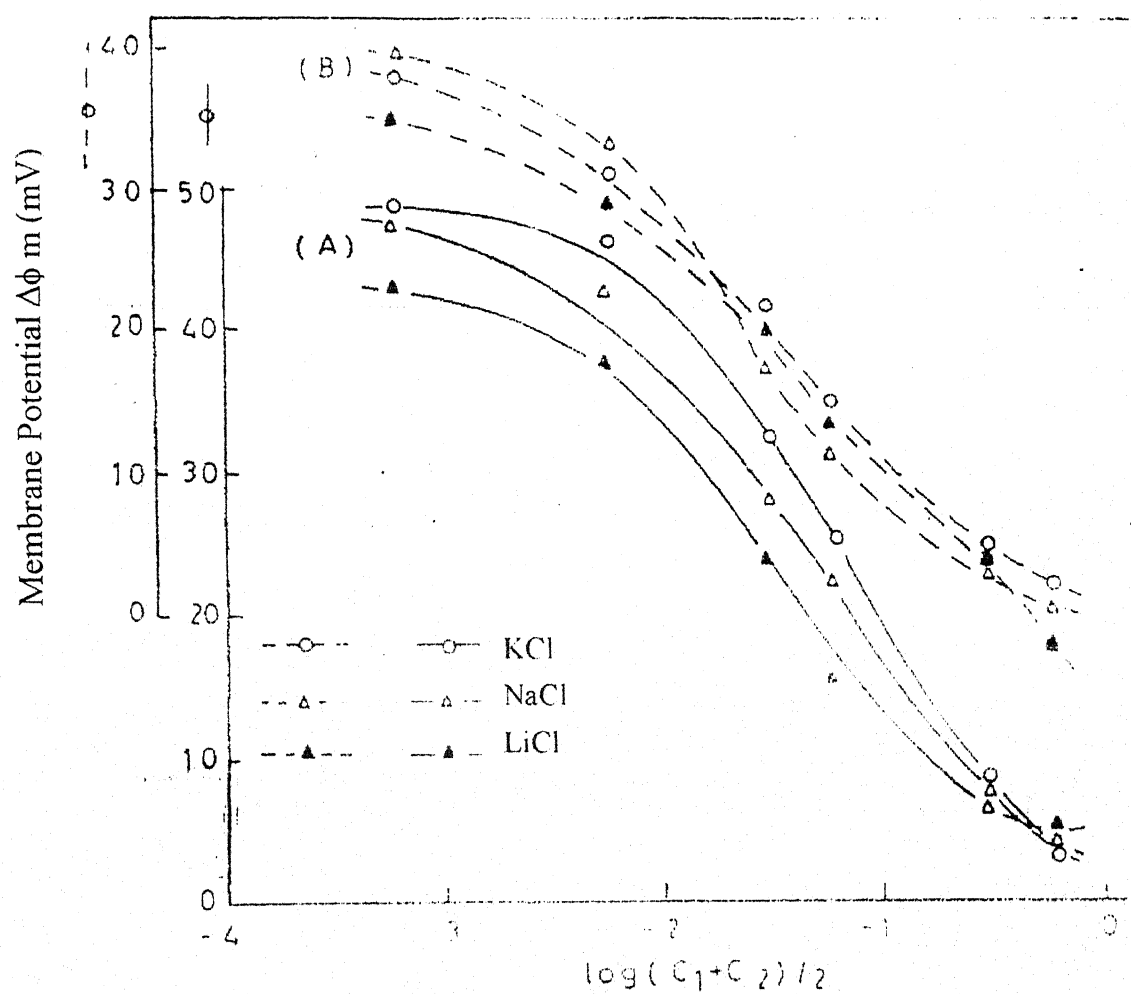


Fig. 3 PLOTS OF OBSERVED MEMBRANE POTENTIALS AGAINST  $\log (C_1 + C_2) / 2$  FOR VARIOUS 1:1 ELECTROLYTES WITH  
 (A) NICKEL PHOSPHATE AND  
 (B) COBALT PHOSPHATE MEMBRANES

**Table 7**

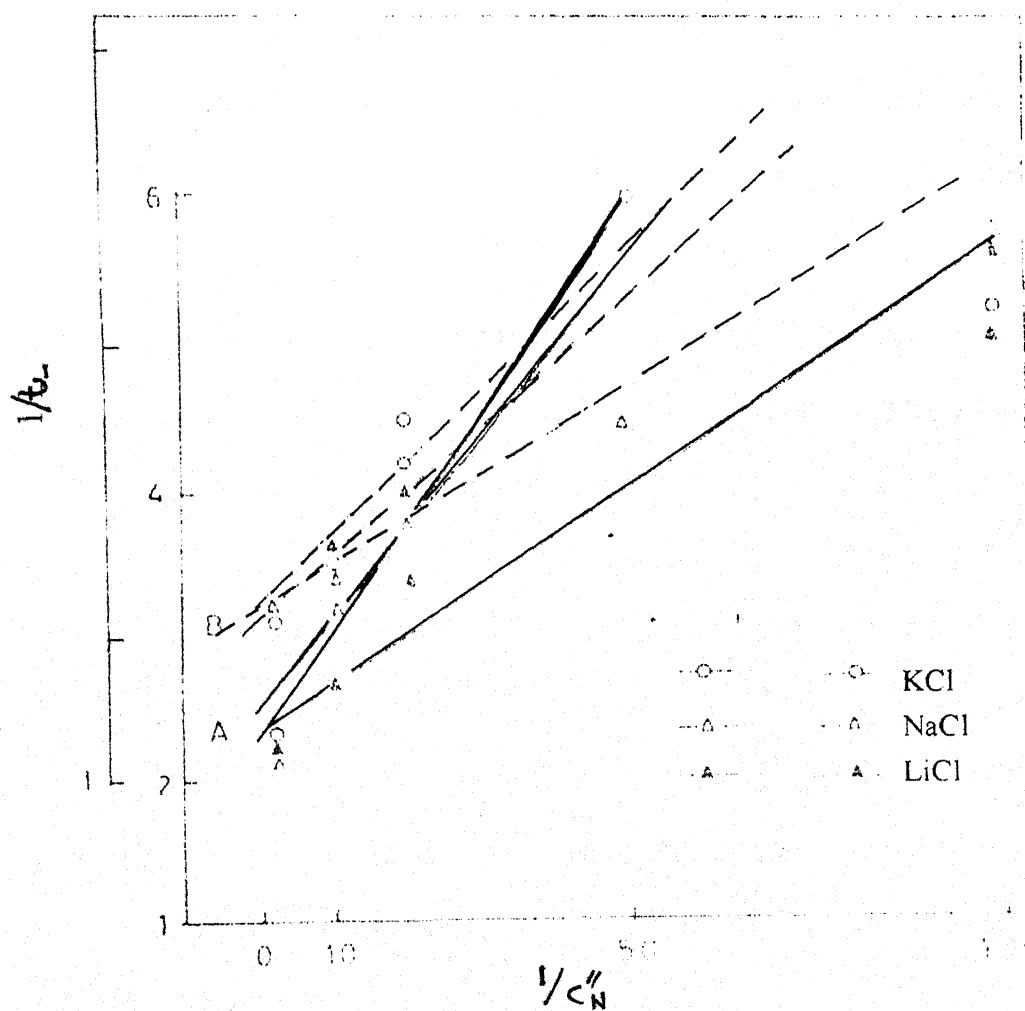
Transference number  $t_-$  derived from observed membrane potentials at various 1:1 electrolyte concentrations at  $\delta=10$  for nickel phosphate membrane.

Electrolyte Pairs Concentrations (mol/l)	KCl	NaCl	LiCl
$10 \times 10^{-1}$	0.473	0.461	0.46
$5 \times 10^{-2}$	0.421	0.433	0.443
$2 \times 10^{-2}$	0.278	0.310	0.364
$1 \times 10^{-2}$	0.218	0.257	0.286
$5 \times 10^{-3}$	0.092	0.135	0.175
$1 \times 10^{-3}$	0.074	0.080	0.127

**Table 8**

Transference number  $t_-$  derived from observed membrane potentials at various 1:1 electrolyte concentrations at  $\delta=10$  for nickel phosphate membrane.

Electrolyte Pairs Concentrations (mol/l)	KCl	NaCl	LiCl
$10 \times 10^{-1}$	0.480	0.490	-
$5 \times 10^{-2}$	0.456	0.474	0.46
$2 \times 10^{-2}$	0.365	0.402	0.377
$1 \times 10^{-2}$	0.310	0.353	0.327
$5 \times 10^{-3}$	0.232	0.206	0.242
$1 \times 10^{-3}$	0.172	0.155	0.194



**Fig. 4** PLOTS OF  $1/L$  AGAINST  $1/C_2$  FOR VARIOUS 1:1 ELECTROLYTES WITH (A) NICKEL PHOSPHATE AND (B) COBALT PHOSPHATE MEMBRANES.

determined. In this way the value of  $V_N$  and  $(\theta/K_N)$  are obtained and are given in Table 9 with various electrolytes for both the membranes.

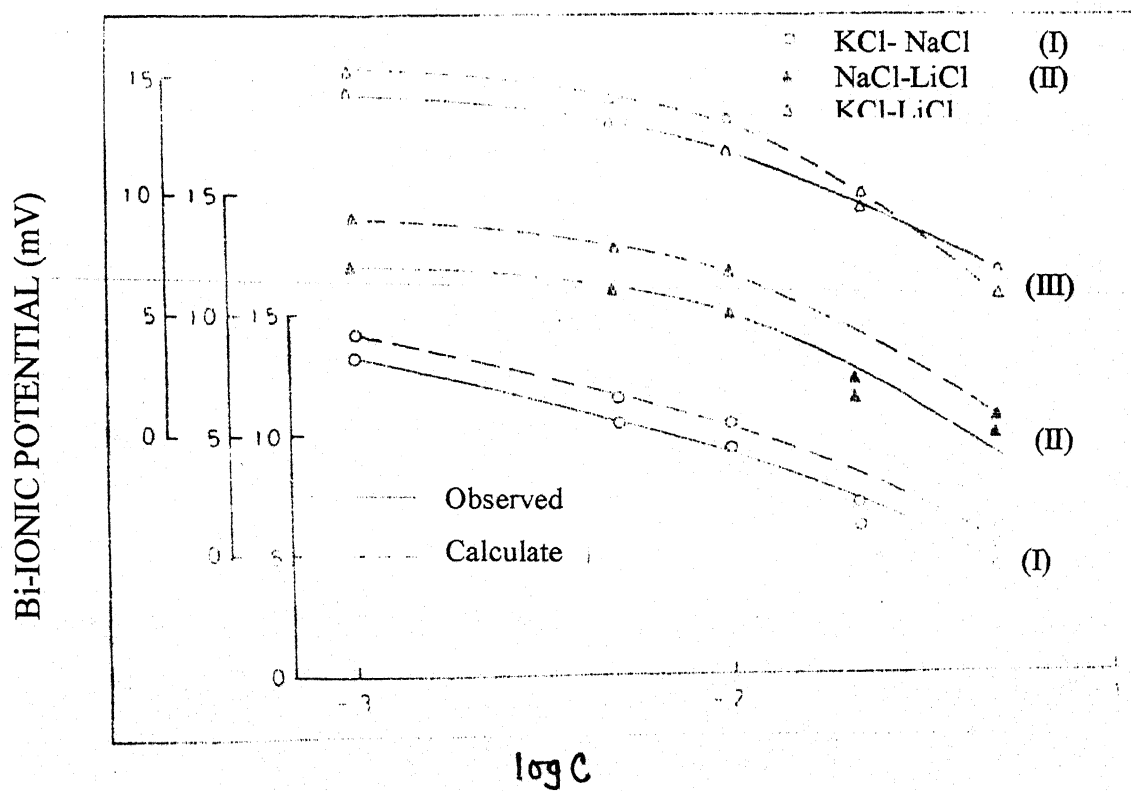
The value of  $G_N$  is calculated from Eqn. 8 by substituting the already determined value of  $(\theta/K_N)$  at different concentrations. By substituting the value of  $V_N(\theta/K_N)$  and  $J$  in Eqn. 5, the theoretical BIP is calculated. These theoretical values of BIP thus obtained are plotted against  $\log c$  and are shown by broken lines in Figures 5 and 6. For comparison the observed values of BIP are also plotted and are shown by solid lines in the same graph. It is quite evident from the figures that the agreement between between the observed and the theoretical value is quite fair and it may be concluded that the theory of BIP developed by Toyoshima et. al. (22) is applicable to our system of parchment supported membranes. Besides of it, it may be said confidently that whatever, limitations were taken for a membrane in the development of the theory of BIP are verified on the behalf of these results.

Table 9

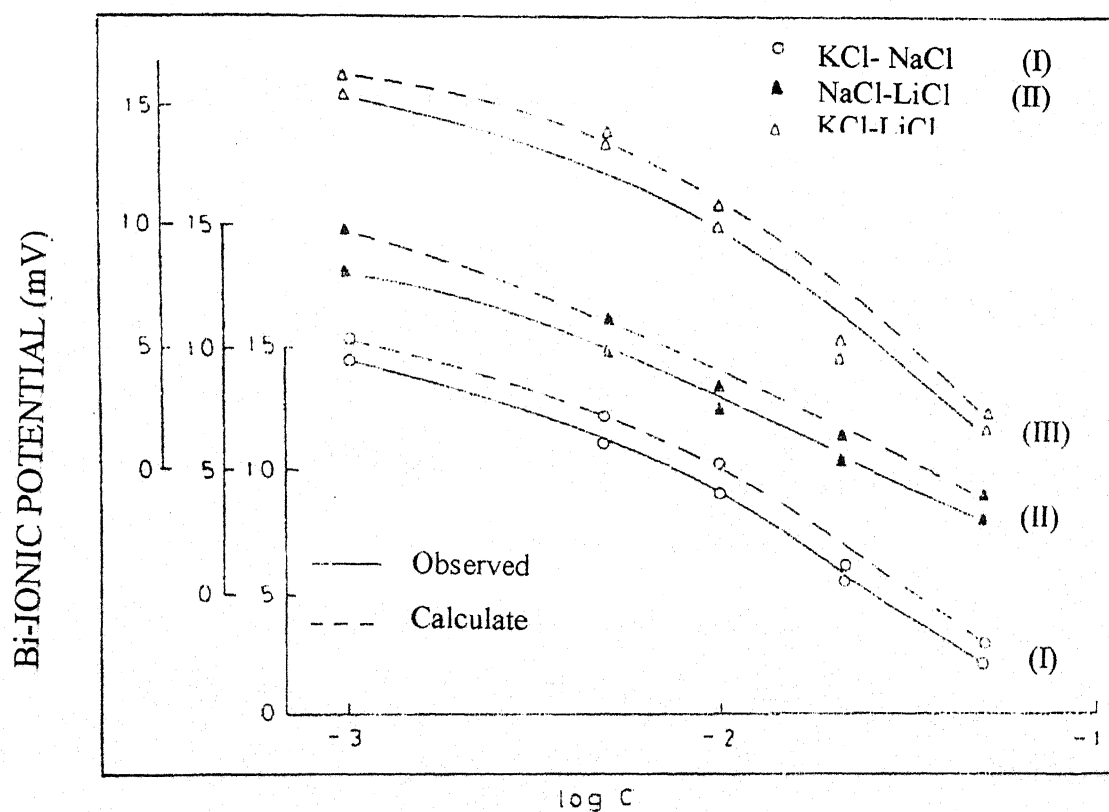
Values derived for parameters  $(\theta/K_N)$  and  $V_N$  for various membrane electrolyte systems at  $\delta = 10$ .

Membrane	Electrolytes	$(\theta/K_N)$	$V_N$
Nickel Phosphate	KCl	0.122	0.45
	NaCl	0.332	2.20
	LiCl	0.059	2.35
Cobalt Phosphate	KCl	0.071	2.35
	NaCl	0.065	2.15
	LiCl	0.048	2.30





**Fig. 5** PLOTS OF Bi-IONIC POTENTIAL AGAINST  $\log C$  FOR VARIOUS PAIRS OF ELECTROLYTES ACROSS NICKEL PHOSPHATE MEMBRANE.



**Fig. 6** PLOTS OF BI-IONIC POTENTIAL AGAINST  $\log C$  FOR VARIOUS PAIRS OF ELECTROLYTES ACROSS COBALT PHOSPHATE MEMBRANE.

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## SUMMARY

Transport phenomena occurring across parchment reported inorganic precipitate membranes have been thoroughly studied on the basis of following aspects, say (i) ionic transport (ii) membrane potential (iii) bi-ionic and multi-ionic potential (iv) electrical conductivity (v) ionic distribution equilibrium and (vi) spatial distribution of ions and the potential within the membranes.

The work presented in the theses has been divided into four chapters:

The chapter - 1, Thermodynamic Irreversibility: What is it ? deals with the detailed explanation of irreversible thermodynamics and mechanics in membrane permeation. Initially, Duhem (1903) referred to irreversibility as one of the most dedicated principle in all types of thermodynamics. At primary stage there were so many confusions for the workers but very soon they were removed after having done hard work. The transport studies of parchment supported inorganic precipitate membranes (i.e. synthetic membranes) are fully based on the principles of irreversible thermodynamics. The kinetic meaning of irreversibility is simple and unambiguous. Initially, the distinction between reversible and irreversible processes was explained by considering the mechanical work done by one fluid on another by taking a typical prototype model involving a gas at pressure  $P_i$  from an external fluid at

different sample kinds of irreversibility.

pressure  $p$ . The differential work done by expanding the gas of volume  $V$  on the external fluid at pressure  $P$  was formulated as:

$$dw = Pdv$$

The expansion process and the work done are said to be "reversible" if  $p$  and  $P$  are equal or nearly equal so that the process can be reversed by a slight change of  $P$ . It is "irreversible" if  $p$  is "substantially greater than  $P$ ". In other words the process is reversible if the gas and the external fluid are kept at or near mechanical equilibrium. If they are far from equilibrium during any substantial part of the process, the process is irreversible.

On the basis of above aspects, the criterion for reversible is more general. A process is said to be reversible, if it can be reversed by a slight change of external conditions. On the other hand, a process is irreversible if, it can not be reversed by a slight change of external conditions. The motion of a particle also describes the criterion of reversibility and irreversibility.

In the discussion of second law of thermodynamics, the emphasis, before considering equilibrium is not only based upon going fluid process but is also going in a particular direction that creates entropy. When the student encounters the second law, he or she is introduced to a "directional" kind of irreversibility. In this way we need to recognize different simple kinds of irreversibility

before we can hope to identify the overall irreversibility of fluid behaviour, i.e., thermodynamic irreversibility.

### **Simple kinds of irreversibility:**

Further, the discussions of irreversibility may be shown in terms of a ball rolling on board (inclined plane). The "external" and "internal" conditions were determined by gravity and the tilt of the board and initial velocity of the ball respectively. From particle (or ball) mechanics it is known that a moving ball has a inertia and its motion can not be reversed immediately by a change of external conditions (tilt of the board). The process has "inertial irreversibility"

Thus, we are led to a criterion for reversibility (irreversibility) that can be stated as follows.

### **Inertial Reversibility**

It was represented by a reversible process, which was actually reversed by a change of external conditions.

### **Directional Reversibility**

A process is reversible if, it can occur in both directions under the prevailing circumstances i.e. it can be reversed experimentally by changing internal conditions without changing external conditions.

### Temporal Reversibility

A process is reversible if it can reverse by reversing the direction of time. The temporal irreversibility can not be ignored as a possible component of thermodynamic irreversibility.

The chapter II of the thesis "Mechanics of Membrane Permeation" is theoretical in which the thermodynamic description of membrane transport is supplemented with the momentum conservation law in the form of the mechanical equilibrium equation. This was possible only after augmenting free solution chemical potential within excess which describes potential interaction between the membrane and permeating species. The theory is applicable for diffusive flows only, although a possibility for its broadening to include viscous flow is indicated. As a test of practical usefulness of the proposed approach, the irreversible thermodynamic description is combined here with the frictional model of membrane permeation. On casting the phenomenological equations into the form of the practical Kedem-Katchalsky equations, it turns out that four practical coefficients are needed in order to determine the three friction coefficients and the partition coefficient.

As only diffusional dissipation is considered and the mechanical equilibrium amply used throughout this report, the theory presented here is applicable only for dense enough membranes which do not allow viscous flow to occur. However, an



indication is given how this restriction can be lifted and viscous flow allowed for. The theoretical description was presented under following heads.

### **Equilibrium thermodynamics and mechanics of membrane permeation.**

In order to obtain a consistent mechanical and thermodynamic description of membrane permeation, author has to supplement the energy balance equations of equilibrium thermodynamics with a mechanical energy contribution.

This was in line with the energy - barrier model which envisaged the membrane just as a potential field  $V(x)$ . Thus the starting equation was the well-known expression for internal energy increment (of small enough volume element) with an additional term  $de^{ext} = F^{ext} dx$ , which described the energy changes due to displacement of the system in an external field of potential forces  $F^{ext}(x)$ , all membrane solution interactions being counted as external.

With membrane belonging to the system under study the another alternative approach to membrane transport was to regard the membrane as an integral part of the system under study. We thus have  $n$ -component mixture (the  $n$ th component being the membrane) with the external force on the membrane only. As it is a mechanical force, we can construct the equilibrium

thermodynamics of our system without taking it into account. The external potential forces on the permeating solution now become internal membrane species interaction. Such interaction is of course, contained in usual chemical potential of the species which could be expressed as:

$$\mu_i(x) = \mu_i + V_i^r P + \mu_i'' + \mu_i'$$

However, it can not be accepted like this because the  $n$ th component of the system, the membrane, differs in that it is a solid phase whose potential can not be expressed by above equation. Moreover, chemical potential of the membrane does not also depend on pressure and on concentration because a membrane equilibrated with a solution does not participate in the overall pressure i.e. its partial pressure is zero and its concentration gradient is maintained by the forces of cohesion to keep the solid phase together under irreversible thermodynamics for membrane permeation" concept.

The permeating solution as the thermodynamic system under study - with allowance for viscous flow, the Irreversible thermodynamics of membrane permeation, like equilibrium thermodynamics, was constructed using either the energy barrier is model conversion or without it. In the first case, the described system is a solution (without membrane) which is acted upon by

external forces of both frictional and potential character. In the later case, the membrane forms an integral part of the system and there are no external forces of friction.

To obtain the irreversible thermodynamics of membrane permeation in the first case it suffices only to modify the usual thermodynamics of free solution by supplementing the momentum balance equation with external forces of friction. The equation has the form

$$\rho \frac{d\bar{v}}{dt} = \text{Div} II + \sum C_i (\bar{f}_i^{\text{exp}} + \bar{f}_i^{\text{fric}})$$

In absence of external forces of friction when membrane forms an integral part of the system, the viscous flow occurs within a membrane and centre of mass can move due to viscous flow independently of the diffusive ion flow. So we can write  $\bar{v} = \bar{v}_d + \bar{v}_v$  where  $\bar{v}_d$  and  $\bar{v}_v$  are diffusive and viscous contributions respectively and fluxes relative to the membrane are :

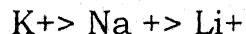
$$\bar{I}_i^a = \bar{I}_i^c + C_i (\bar{v}_d + \bar{v}_u)$$

Irreversible thermodynamics combined with the frictional model and taken into account for treating the membrane and permeating solution as a system it was found that it does not interact frictionally with the surroundings. The author can write the dissipation function in the form of a number of equations during

the substitution and elimination of various factors in the equations obtain at the time of simplifications. Thus combining the irreversible thermodynamic. descriptions with the frictional model of membrane permeation, more important practical results were obtained.

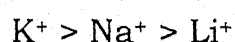
Chapter III, "Metal Ion Selectivity of Membranes" of the thesis describes the determination of selectivity of the parchment supported nickel phosphate and cobalt phosphate membranes for metal ions of the electrolytes.

Initially on the basis of the values of membrane potential observed experimentally across both the membranes, selectivity sequence of metal ions was found as :

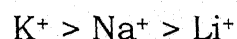


Some theoretical equations based on the principles of non equilibrium thermodynamics derived by Kobatake and co-workers for the charged membranes were used to evaluate the values of effective fixed charge density of the membrane electrolyte system. Involving the membrane potential measurements in these equations, various thermodynamic membrane parameters were also evaluated and with the use of these parameter the effective fixed charge density values against 1: 1 electrolytes of both the membranes were evaluated. The values of apparent. transference number  $t_{app}$  and the permselectivity  $P_s$  have been important factor

during the electrochemical characterization of the membranes. Another theory developed by Taska and co-workers has also been used in the evaluation of magnitude of fixed charge cpx. Since the values of cpx thus obtained were quite low and the membranes were expected to have low electrostatic field strength of the fixed charge sites. For this reason, following the Eisenman: and Hom selectivity sequence of metal ions was proposed



In bi-ionic method, the values of bi-ionic potential across both the membranes using various combinations of 1: 1 electrolytes at different concentrations were measured. The intramembrane permeability ratio values of cations were obtained by plotting method. conductivity values of the membranes were observed experimentally in order to evaluate selectivity of the membranes using predetermined values of the intramembrane permeability ratio. The sequence of selectivity of metal ions in both the membranes separately was obtained as:



which on the basis of Eisenman sherry model of membrane selectivity point towards the weak field strength of charge groups attached to the membrane matrix. Perfect Donnan exclusion of

coions was realised in the dilute limit of the external solution.

The mixture method was used to assess the selectivity sequence of the membranes for the cations by evaluating the values of potentiometer selectivity constant  $K_{ij}^{pot}$  of the membranes. In this method a set of mixture response for both the primary ions i.e. i and j on one side while varying the concentration of ionic species i and j on the other side. The values of  $K_{ij}^{pot}$  were derived by using slope of the lines which were obtained as a curve between electrical potential  $\Delta E_i$  or  $\Delta E_j$  and  $\log a_i$  or  $\log a_j$ . Thus, on the basis of  $K_{ij}^{pot}$  values the selectivity sequence of metal ions was tested. Further, the selectivity of metal ions of the membranes was also tested in terms of the values of various activation parameters like:  $E_a$ ,  $\Delta P^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$ , which were predicted on the basis of rate theory. In the mechanism,  $\Delta S^\ddagger$ , the entropy of activation represents the mechanism of ion permeation in terms of electrolyte diffusion with partial immobilization in the behaviour of membrane for metal ions. Thus the selectivity sequence of metal ions of the membranes following both of these methods was found.



In the present IV chapter, "Biionic Potential studies" of the thesis, two different ions in different sets were used for membrane characterization. Bi-ionic potentials (BIP) and membrane potentials

arising across nickel phosphate and cobalt phosphate membranes using various combinations of 1:1 electrolytes i.e. (KCl-NaCl, NaCl - LiCl, KCl-LiCl) at different concentrations have been measured. The values of intra membrane mobility ratio were calculated using the methods suggested by Wyllie and Kanaan.

Recently Toyoshima and co-workers have derived theoretical equations for the membrane potential as well as for biionic potential. The applicability of this theory was tested using both the phosphate membranes of nickel and cobalt respectively. In the derivation of the bi-ionic potential equation, it is most critical to assume that the activity coefficients and mobilities of small ions in the membrane phase are given by the expression proposed from the expanded "addictively rule". Toyoshima's theoretical equation for bi-ionic potential contains four parameters namely (i)  $Q/KN$ , (ii)  $VN$ , (iii)  $GN$  and (iv)  $J$ . These parameters were evaluated for both the parchment supported membranes of nickel phosphate and cobalt phosphate separately. Substituting the values of these four parameters in the desired equations, the values of theoretical biionic potentials were calculated at different concentrations. These were compared with experimentally observed values of biionic potential. It was found that the theoretical and observed values of bi-ionic potentials were closer to each other thereby confirming the applicability of Toyoshima's equation to this system of parchment supported phosphate membranes of nickel and cobalt transitional metals respectively.

**PUBLICATION**

1. R.S. Kushwaha, Anil Kumar & R.B. Sharma; Studies with model membrane Test of various theories in the evaluation of membrane selectivity from electrical potential and conductivity measurements **Flora & Fauna Vol. 7 No. 1, 9-14 (2001).**
2. R.S. Kushwaha, R.B. Sharma, Manoj Kumar and M.A. Ansari; Studies with model membranes: Evaluation of Thermodynamic parameters and testing of theories of membrane and bi-ionic potential based on irreversible thermodynamics. **Flora & Fauna (2005) In Press.**